Memorandum

Respondent

I

M E C A N I Q U E S T A T I S T I Q U E

Notes on lectures by

Prof. L. ROSENFELD

Department of Physics
University of Manchester

Delivered at the Ecole d'Eté de
Physique Théorique, Les Houches, FRANCE
28 Juillet - 28 Août 1952

INTRODUCTION

1.- Aim and scope of statistical thermodynamics.

The aim of "statistical thermodynamics" is to give an atomistic interpretation of heat phenomena. In the first phase of its historical development, the atomic conception was restricted to the structure of ponderable matter and the atomistic treatment of thermal properties of matter accordingly became known as "statistical mechanics". Later on, however, the phenomenological concepts and laws of thermodynamics were extended to radiqtion phenomena, and the interpretation of these phenomena in terms of electromagnetic fields provided the basis for a statistical treatment of the thermodynamics of radiation on quite the same lines of that of matter. It seems therefore advisable to replace the traditional denomination of "statistical mechanics" by a name which indicates more correctly the wider scope of the theory.

In its broadest aspect, the atomistic view of matter and radiation consists in regarding these physical agencies as composed of elements - the atoms (or molecules) of matter and the monochromatic waves of electromagnetic radiation - obeying well-defined laws of motion or propagation. The physical quantities describing the properties of macroscopic observation are then interpreted as average values of corresponding atomic, or elementary, quantities, taken over large numbers of constituent elements. Macroscopic relations between physical quantities can then in principle be derived, by suitable averaging processes, from the elementary laws of motion or propagation. In itself, the taking of averages involves only a trivial use of statistical conceptions. But just in the analysis of heat phenomena such conceptions are found to play a quite essential part and their introduction into the atomistic picture thus appears as a deep-lying feature of the whole theory.

2.- Statistical aspect of the second law of thermodynamics.

The central problem is the interpretation of the second law of thermodynamics. This law can be conveniently analysed into two

statements, relating to controlled (quasi-statisc) and spontaneous transformations respectively :

(a) there is a quantity called entropy which belongs to each state of thermal equilibrium state of the system in a controlled way is a well defined function of the thermal parameters characterizing the transformation ;

(b) if a thermally isolated system undergoes a spontaneous transformation from one state of equilibrium to another, its entropy increases, thus indicating the irreversible character of the transformation.

Now, the essentially statistical aspect of entropy and thermodynamical irreversibility is well illustrated by such processes as the mixing of two gases. For the increase of entropy in this case, when considered from the atomistic point of view, can only appear as a function of the numbers of atoms involved in the mixing processes : in fact, it is simply related to the greater probability of the disordered state represented by the mixture, as compared with that of the separated gases. But more generally, it is found that heat in its various manifestations must be regarded as the result of some disordered form of motion or propogation of the elementary constituents. Entropy is a statistical measure of this disorder, and its increase expresses a transition to a state of greater probability.

However, it is important to realize that entropy is a statistical concept of a very specific kind : it expresses a definite relation between statistical and thermal characteristics of the system. In other words, the statistical element is introduced into the definition of entropy by the fact that one considers only thermal transformations of the system performed in a quasi-static, i.e. macroscopically controlled, way. This physical aspect of the entropy concept is not always properly appreciated in the so-called theory of information. Entropy is indeed a measure of a certain type of "information" pertaining to the microscopic state of the system ; but it only refers to that information which can be obtained or lost by operations involving exchanges of heat between the system and other bodies (or, in particular, keeping the system thermally isolated). The statistical aspect of thermodynamics thus arises from the fact that the definition of the macroscopic states of the system entails a limitation of our control of the microscopic

behaviour of its elementary constituents.

It is just this circumstance which leads to the irreversible thermal evolution of an isolated system when its atomistic elements are left to follow the course determined by their own laws. The derivation of this fundamental property is the oblect of the " ergodic theorems" which forms the backbone of statistical thermodynamics. Asymptotic irreversibility is a very general feature of statistical "chains" of events : it is exhibited by results of lotteries just as well as by assemblies of atoms. It is especially remarkable in the latter case, however, in view of the reversible character of the elementary laws of motion : the conciliation (in a statistical sense) of macroscopic irreversibility with microscopic reversibility is the essential achievement of the statistical analysis of the second law of thermodynamics by means of the ergodic theorems.

3. Statistical thermodynamics and quantum theory.

In the preceding general outline of statistical thermodynamics, the exact nature of the atomic systems and radiation fields considered has been left open. It is well-known that, when one attempted to describe them in terms of ordinary mechanics and electromagnetic theory, the resulting thermodynamics led to serious inconsistencies : this was in fact the origin of the discovery of the quantum of action and of the ensuing development of the quantum theory of both radiation fields and atomic systems.

It is clear, therefore, that in order to obtain a consistent formulation, we must take as basic assumption the quantal description of the elementary constituents. But it should be equally clear that this does not make the least difference for the fundamental argument of statistical theory, outlined above. Since the quantal laws, just as the classical ones, are essentially reversible with respect to time, the problem of deriving the macroscopic irreversibility by introducing a suitable statistical element into the theory remains unchanged and is again solved by ergodic theorems.

The present course will take as its leit-motiv the complete parallelism, in regard of the general structure of the theory, between

classical and quantal statistics of atomistic systems. A special emphasis on this aspect of the subject is needed, because it has not always been clearly recongized. The issue has been obscured by the fact that quantum theory itself, in contrast to classical theory, introduces a statistical element at the miscroscopic level ; and it has sometimes been confusendly argued that it is the elementary quantal statistics which provides the basis of macroscopic irreversibility. In reality, we have here two completely distinct statistical features, which are not only logically independent of each other, but also without physical influence upon each other. The question whether the elementary law of change is deterministic (as in classical physics) or statistical (as in quantum theory) is entirely irrelevant for the validity of the ergodic theorems.

The thermodynamical irreversibility is thus related, not to any statistical feature of the elementary systems, but to another, quite independent, statistical feature, which specifies the point of view of the macroscopic pbserver. It is interesting to note that the logical relationship between the macroscopic and microscopic modes of description of the system is one of complementarity, in the sense that the two points of view are mutually exclusive : a complete knowledge of the microscopic state of the elementary constituents precludes the use of such macroscopic concepts as temperature and entropy ; conversely, the macroscopic description implies a statistical indeterminacy in the knowledge of the microscopic state. But this complementarity must be carefully distinguished from the similar relation between conjugate quantities pertaining to the elementary quantal systems.

While it is important to realize the essential identity of structure of classical and quantal thermodynamics, it is no less necessary to keep in mind the main points of difference between the two theories :

(a) as already stated, the concrete consequences of quantal thermodynamics, while containing those of classical theory as limiting cases, are free from the inconsistencies of the latter. The law of equipartition of energy, which is the source of these inconsistencies, is in fact reduced to a law of asymptotic validity. There are well-known examples of

systems whose behaviour even under ordinary experimental conditions illustrates extreme cases of quantal statistics : the pure radiation field on the one hand, the metallic state of matter on the other.

(b) There is in quantum theory a type of irreversible process unknown to classical theory : the measuring process. The measurement of a certain quantity pertaining to a system may involve an irreversible change of state of the system, with a corresponding increase of entropy.

(c) From a more formal point of view, the development of statistical thermodynamics on the basis of the quantal laws is neater than on the assumptions of classical theory for the elementary systems. The proof of the ergodic theorems, in particular, is somewhat easier. But the main advantage of quantum theory is that it makes possible, in a much more compendious way than classical theory, a unified treatment of both matter and radiation (and in fact of any physical system whatsoever). This is, of course, a consequence of the elimination of the dualism between matter and force and its replacement by the conception of the complementary manifestations of particle and field for every constituent of the physical world.

:.- Outline of the fundamental argument.

In order to bring out the similarities and differences just enumerated between classical and quantal thermodynamics, it will be necessary to present the fundamental argument successively from each point of view. This we shall try to do with a minimum of repetition by first giving a full treatment of classical theory and then going more rapidly over the argument again on the basis of quantum theory, just stressing the points of agreement and difference.

The argument may be conveniently divided into three parts :

(1) : The first part, which is of a preparotory character, is concerned with isolated systems. The systems of actual interest are usually not isolated, but they can always be conceived as embedded in a larger system, which may be treated as isolated to any desired approximation (just by making it large enough). Once the statistical treatment of isolated systems is developped, that of actual physical systems in interaction with their surroundings can be derived from it by studying the behaviour of a small part of an isolated system.

The interactions of a physical system composed of a large number of elementary constituents with its surroundings are of two kinds ; there are dynamical interactions, involving exchange of energy, momentum and angular momentum; there is also a flow of the atomic constituents themselves into and out of the system, with an accompanying exchange of mass and perhaps electric charge or other substantial properties. Strictly speaking, the two types of exchange cannot be separated; in particular, according to quantum theory, no physical system in interaction with others can be regarded as chosed, i.e. as having a fixed number of elementary constituents. However, the concept of closed system is, of course, quite a useful approxilation in many cases, and it is convenient to study such systems first.

(2) The second part of the theory will accordingly be devoted to closed systems in dynamical interaction with their surroundings. It will be sufficient to restrict the analysis to the exchange of energy, which is the only one of interest for the theory of heat, and which is typical of the kind of treatment to be applied to other dynamical processes when necessary. It is, in fact, by considering energy exchanges that the concept of temperature can be defined : if we want to give any system a definite temperature, we must bring it in thermalcontact with a "thermostat", i.e. allow it to exchange energy with a system of sufficiently large heat capacity to maintain its temperature constant to any desired approximation. We may then regard the total system formed by our closed system and the thermostat as an isolated system. From the statistics of the total system that of the closed system is then derived by eliminating the atomistic variables pertaining to the thermostat and reducing the representation of the latter to a single macroscopic parameter, which plays the part of the temperature.

(3) The method just oulined for taking account of the dynamical interactions of closed systems with the surroundings can immediatly be extended to the exchanges of elementary constituents between the system and its surroundings.. This is the third and last stage of the theory; it is concerned with open systems, i.e. systems with an indefinite number of elements. The procedure consists in treating an open system as a small part of a closed system, which forms so to speak a reservoir of elements of all kinds taking part in the exchange. The elimination of the variables pertaining to the reservoir yields a statistical distribution

function for open systems, containing macroscopic parameters related to the average numbers of elementary constituents present in the systems.

Let us know take up in succession the three stages of the theory and consider the argument a little more closely in each of them.

5. - Isolated systems : the ergodic theorems.

Consider the evolution of an isolated system in the course of time from a certain instant at which all connections with the surroundings have been severed. We know that after a period of adjustment, or "relaxation", it will tend to a stationary state in which it will persist indefinitely. From the atomistic point of view, the value of any macroscopic quantity pertaining to the system will be interpreted as the average of a definite microscopic qiantity over the interval of time necessary for the measurement. Such a time interval may be extremely short in the macroscopic scale and yet cover the passage of the system through a large number of successive microscopic configurations : it is then called "physically infinitesiaml". In the present case, the time average will be the same over any interval, except perhaps during the period of relaxation : the macroscopic value pertaining to the stationary state of the system may thus be represented by an average extending over an infinite time, an idealized concept which turns out to be more amenable to a general analysis. In fact, this average over infinite time embodies all the microscopic configurations actually taken by the system but is obviously independent of the order in which they have been successively taken : it is therefore equivalent to a definite statistical average, i.e. an average defined by a distribution law indicating the relative frequencies of occurence of the various configurations of the system in the course of its evolution. Such a statistical distribution law, fromwhich the time has disappeared completely, characterizes the stationnary state of the isolated system. The derivation of the distribution law for the isolated system is thus the fundamental problem of statistical thermodynamics.

The above argument, however, is incomplete in as much as it takes for granted the empirically observed irreversible tendency of the isolated system to a stationnary state. This behaviour, as already

pointed out, is by no means obvious in view of the reversibility of the elementary law governing the change of configuration of the system with time. The first task is therefore to define the precise meaning of the macroscopic irreversibility, i.e. to find the conditions under which the time average of any quantity pertaining to the system exists independently of its initial state. This is the object of the ergodic theorems. It then turns out that the solution of the second problem, viz. the determination of the statistical average equivalent to the time average, is an immediate consequence of these theorems.

At this stage, it will be necessary for the first time to make a distinction between classical and quantal systems. We must first describe more accurately in each case what we have hitherto loosely called a "configuration" of the system.

A configuration or phase of a classical system at any time is given by a set of values (p_t, q_t) of the 2f canonical variables describing the system. Such a set corresponds to a point in a Cartesian 2f-dimensional phase space.

The temporal evolution of the system from any given initial phase is represented by a well-defined trajectory in phase space, corresponding to a unique solution of the Hamiltonian equations of motion.

This trajectory remains on a surface of constant energy in phase space : this expresses the condition that the system be isolated. Morever we shall make the essential assumption that all the phases of our

A configuration or state [+] of a quantal system at any time t is described by a wave-function $\Psi(q,t)$ depending on a set of variables q. This wave-function corresponds to a vector in a functionnal Hilbert space.

The temporal evolution of the system from any given initial state is represented by a well-defined precession of the state vector in Hilbert space, corresponding to a unique solution of the Schrodinger wave equation.

Owing to thenperturbation involved in the operation of isolating the system, the initial state -

+ To avoid confusion with the macroscopic states of the system we shall when necessary speak of atomistic states.

system are confined to a finite region of phase space.

Birkhopp's fundamental ergodic theorem states that the time average of any quantity exists for almost all trajectories on any energy surface. The condition for the time-average to be independent of the initial phase is expressed by a certain topological property of the trajectory, which can be very roughly described by saying that the trajectory is not confined to a part of the energy surface but in a certain sense covers the whole of its surface.

vector will in general not coincide with any of the eigen-vectors of the energy of the isolated system, but will be expressed as a superposition of these eigen-vectors with definiteamplitudes and phases.

It is easy to see that the time-average of any quantity exists in any state of the system. The condition for the time-average to be independent of the initial phases is that there be no degeneracy of the energy of the system.

This condition mainly excludes the existence of other uniform integrals of the motion of the system than the energy

A system, for which the above condition is fulfilled for almost all trajectories will therefore exhibit the characteristic irreversible behaviour of macroscopic experience, provided that the determination of the initial state in which it is isolated from its surroundings, is sufficiently inaccurate to prevent the exceptional trajectories from "showing up". In other words, we are not

A system for which the above condition is fulfilled will therefore asymptotically exhibit the behaviour of a statistical mixture of its stationary states (i.e. eigenstates of its energy). The coefficients of the mixture are the squares of the amplitudes of the corresponding eigenvectors in the initial state : the statistical mixture is thus seen to arise from the act of isolating the system

interested in following up the system along any particular trajectory, but as part of the definition of the macroscopic (initial) state of the system we introduce a statistical uncertainty in the initial phases. The macroscopic time-average is obtained as a result of this additional averaging over the initial phase, which has the effect of wiping out the possibility of finding the system just on an exceptional trajectory.

Since any phase can of course be regarded as a possible initial one, we must extend the statistical uncertainty of phase determination to the whole region of phase-space occupied by the trajectories. We thus see that the statistical average equivalent to the time-average must not be conceived as taken over the energy surface as a mathematically continuous multiplicity of phases but over a coarse subdivision of this surface into finite "cells", representing the physically infinitesiaml domains allowing for the uncertainty of phase determination. The ergodis law of distribution which characterizes the isolated system, and which is immediately derived from Birkhoff's theorem, actually refers to this coarse distribution on the energy surface.

from its surroundings, and thus to introduce the macroscopic element in the definition of the isolated system.

One may say that this corresponds to a certain "coarseness" in the determination of the energy of the isolated system. The ergodic law of distribution of an isolated quantal system, which is directly given by the above statistical mixture, actually refers to this coarse distribution over the energy of system.

Of course, the particular way in which the coarseness is introduced (the mode of subdivision of the energy surface into "cells") is largely arbitrary. For purposes of calculation, it will even be allowed to ignore it, i.e. to treat the cells as mathematically infinitesimal; but it is essential to remember that one is actually dealing with a coarse distribution in order to cope successfully with all paradoxes raised by the concept of irreversibility.

Of course, the particular way in which the coarseness in introduced (the choice of the amplitudes of the energy eigenvectors in the expression for the initial state vector) is largely arbitrary. It will not enter into any actual calcualtion, but though purely formal its introduction is quite essential for the consistency of the argument.

A convenient way of expressing the coarseness of the energy determination is to divide the succession of eigenvalues of the energy into neighbouring groups, or "shells" all members of which are attributed the same weight (i.e? amplitude.)

The ergodic theorem just discussed is so to speak the core of statistical mechanics. As already stated, the distribution laws for closed systems (and open) are ultimately based upon it. But as it stands, it does not quite cover all cases of isolated systems which may be of interest and it needs an extension for this purpose both in the classical and in the quantal case. It will be noticed that although the argument in the two cases run quite parallel to each other, there is in the final step a certain discrepancy.

The classical treatment of the isolated system leads to a "coarse" but detailed distribution among the phases of a sharply defined energy surface.

in the quantal treatment of the isolated system, a statistical distribution over the energies is obtained, which gives no information whatever over any distribution over "phases" defined by the dynamical variables of the system.

It is possible, however, to restore the parallelism completely and to establish a second ergodic theorem which has now the same form in the two cases . To this end,

let us, in the classical case, extend the definition of a (macroscopically) isolated system by allowing a certain "coarseness" in the definition of its energy also. Instead of considering a "cell" of initial phases on an energy surface this amounts to considering such a cell in an energy "shell", i.e. in a domain of phase space comprised between two neighbouring energy surfaces. The second ergodic theorem due to Hopf, states the conditions for the existence of a time-average under these more general circumstances. For almost all pairs of energy surfaces within the shell we must have ergodicity not only on each of them, but also on the composite surface formed by them in the 4f-dimensional phase space obtained by taking together two identical sets of variables $(q^{(1)}, p^{(1)}; q^{(2)}, p^{(2)})$ Moreover, the existence of the asymptotic time average must now be understood in the sense of convergence in the mean : what we can prove is only that the time average of the fluctuations tends to zero as the time interval over which it is taken increases indefinitely.

we must try, in the quantal case, to define an analogue to the cell subdivision of phase space of the classical theory. The notion of phase space has of course no meaning in quantum theory, since the q's and p's are not commutable. But it is always possible to construct some set of quantities Q, P which do commute between themselves and also with the energy, and which can thus be used to define a subdivision of the energy shells already introduced into smaller"cellles". We may then study the fluctuations in the course of time of the expectation values of the quantities Q,P (or any function of them). As shown by Von Neumann, an ergodic theorem entirely similar to Hopf's can be enunciated for these fluctuations : their time average over increasingly large intervals tends asymptotically to zero.

The value around which the fluctuations occur, and which thus represents the asymptotic time average of the quantity considered, appears in the form of a very simple statistical average : it corresponds to a uniform coarse distribution over the cells of an energy shell ; i.e. the relative statistical weights of these cells are given by

their volumes in phase space.	their degrees of degeneracy with respect to the energy.

We thus arrive at the following general picture of the statistical behaviour of isolated systems. The macroscopic concept of isolating the system from its surroundings is represented by the introduction of a "coarse" subdivision of "phase space" into cells. The precise mode of subdivision is irrelevant ; the only characteristic of the cells entering into the fianl result is their weight, defined either by their classical phase space volume or their quantal energy degeneracy. The second ergodic theorem then asserts the equivalence (in the sense just explained) of the asymptotic time average with a statistical average, corresponding to a uniform coarse distribution over the cells of an energy shell.

It is clear that the distribution law derived from the first ergodic theorem is a limiting case of the law just enunciated. Although the latter is both simpler and more general, the former nevertheless finds a more direct application in important cases, and it is essential to keep in mind the distinction, sometimes not clearly realised, between the first and second ergodic theorems.

6.- Closed systems : the canonical distribution.

A closed system, interacting with a "thermostat" is not limited to any energy shell ; its statistical distribution law will extend over the whole domain of its possible atomistic states, and will in particular assign definite statistical weights to the different energy shells. The mechanism by which the closed system isdistributed in energy is its exchange of energy with the thermostat, and the resulting distribution law will thus depend in some way on quantities describing the state of the thermostat. Our aim will now be to show that

the thermostat is represented in the statistical law for the closed system by just one parameter, whose physical significance is directly related to the concept of temperature.

The argument, due to Boltzmann, is quite straightforward : the total system consisting of the closed system and the thermostat is regarded as isolated and its ergodic law of distribution, as given by the first ergodic theorem, is considered. Although it is quite essential for the whole argument that there should exist an interaction between the closed system and the thermostat, it is immaterial how large this interaction is; it is therefore permissible to assume it to be infinitesiaml in comparison with the energy content of both the closed system and the thermostat. The energy of the total system is thus the sum of the energies of the two component parts; the ergodic distribution of the total system accordingly takes the form of an integral over all divisions of the total energy into two parts, and to each such division corresponds a statistical distribution which is a product of two factors, pertaining to the closed system and the thermostat, respectively. The form of the"law of composition" of the distribution in energy of the two components of our system allows a direct application of the central limit theorem of the calculus of probabilities, which yields the asymptotuc form of the distribution of energy of any small part of the total system. This has the well-known expression called the Boltzmann or canonical distribution ; the thermostat is represented in it only by a parameter, called the modulus of the distribution; which is related to the energy of the total system and is interpreted as the absolute temperature (in dynamical measure). Moreover, the distribution depends on the macroscopic parameters defining the external conditions to which the closed system is subjected (e.g. the volume of the container if it is a gas).

The knowledge of the distribution law suffices, in principle to derive all the macroscopic properties of the closed system in terms of its temperature and external parameters. In fact, it is a well-known consequence of the two laws of thermodynamics that there exists a characteristic function of any set of macroscopic cariables, representing the various physical aspects of the system from which all the other quantities can be derived. If the set of variables consists of the tempe-

rature and external parameters of the extensive type (such as the volume), the characteristic function is the free energy of the system. Its expression in terms of the canonical distribution law is readily established; the procedure being to verify that the proposed statistical expression has the characteristic properties of the free energy, i.e. that its variation in a quasi static transformation of the sytem has the expected relation to the work done and heat exchanged in the transformation. In isothermal transformations, the variations of free energy gives directly the amount of work yielded by the system, a quantity which can be immediately expressed in terms of statistical averages. The case of a diabatic transformations is more delicate, since it involves the isolation of the system from its environment ; the effect of a change of the external parameters on the statistical distribution of such an isolated system requires careful investigation. It can be shown, however, that the distribution remains canonical, with an appropriate variation of its modulus. It then becomes apparent that the corresponding variation of the free energy with respect to the modulus is that given by Helmholtz' formula. This completes the identification of the statistical expression dor the free energy, i.e. the statistical foundation of thermodynamics, so far as reversible processes are concerned.

Owing to the choice of temperature as the fundamental thermal parameters, the entropy does not enter explicitly into the preceding considerations. It can be derived in the usual way from the free energy, and its statistical expression is found to be very simply related to the canonical distribution density : it is, apart from the sign, the canonical average of the logarithm of this density. If now the system undergoes an irreversible transformation, the initial distribution density will differ in an arbitrary way from the canonical form corresponding to the final values of the parameters, and the initial entropy, with the mimus sign, will appear as the average logarithm of this arbitrary distribution density. By taking account of the monotonic character of the logarithm function, it can be shown that such an average logarithm of a distribution density is always larger than that corresponding to the canonical distribution in the final state of the system. The law of increase of entropy is thus obtained as a consequence of the statistical expression for the entropy.

7.- Open systems : the chemical potentials.

It will be seen that the argument leading to the canonical distribution law for closed systems is essentially concerned with the statistical distribution, between the various parts of a large system, of a quantity, the energy, which satisfies a law of conservation and a law of additivity. These two properties are all that is needed for the application of the central limit theorem which directly gives the asymptotic distribution law. It is clear, therefore, that the same argument can be immediatly extended to open systems, since the quantities whose distributions have to be considered in this case ; the numbers of constituent elements of various kinds, have the two required properties. Moreover, just as in the case of energy exchanges for closed systems, the abstract argument is exactly adapted to a clear physical situation, viz. the exchange of elementary constituents between the system considered and its surroundings, which play the part of an arbitrarily large reservoir of such constituents.

The distribution law for the number of elements of any kind has thus a form very similar to the canonical distribution law for the energy ; in fact, it arises from a Poisson distribution around an average value of this number of elements. For each kind of element, a new macroscopic parameter thus appears, related to the average number of elements in much the same way as the modulus of the canonical distribution is related to the average energy; it is readily interpreted as the chemical potential introduced by Gibbs in the thermodynamics of open systems.

In dealing with systems of identical elements, one must observe that a microscopic state of the systems is physically determined by the set of values of the variables pertaining to all the constituent elements, irrespective of the individuality of these elements. Thus, two microscopic states differing only by some permutation of the groups of variables belonging to the various elements are physically indistinguishable. To express this fact, Gibbs introduced a distinction between specific and generic phases : a specific phase is defined by the assignment of the values of the variables for each individual element ; a

generic phase is the set of specific phases corresponding to the same values of all the variables. In classical statistics, it is quite essent ial to take into account the distinction between specific and generic phases in all questions in which the numbers of elements of the systems occur explicitely, as in the thermodynamics of open systems or in the estimate of the time of relaxation neccessary for the establishment of statistical equilibriul. Many confuse and inconclusive discussions arose from the failure to pay sufficient regard to this point. In quantal statistics, on the other hand, all such difficulties vanish, since qunatum theory only deals with generic phases.

The quantization of the numbers of elemrnts gives rise to novel aspects of the statistics of open systems. It is well-known that this quantization obeys very different rules according as the elements in question are fermions, subject to the exclusion principle, or bosons satisfying a principle of symmetry. The general distribution law for open systems accordingly predicts very different behaviours for systems of fermions or bosons. The corresponding theories are usually called Fermi-Dirac and Bose-Einstein"statistics"; it should be clear that the statistical basis of these theories is the same, the difference arising from the specific properties of the elementary constituents in each case.

CLASSICAL STATISTICS

I.- General properties of Mechanical systems

1.- Notion as i somorphism in phase-space. We consider a mechanical system, the state of which is described by f generalised coordinates. q_1 and their conjugate momenta p_i. The set (q_i, p_i) $i = 1,\ldots,f$ defines a point P in a 2f-dimensional phase space, to which we assign for a reason soon to become apparent, a euclidean metric. The measure of an element of phase-space is accordingly defined as its euclidean volume $d\mu = dq_1 \ldots dq_f\, dp_1 \ldots dp_f$.

The succession of states occupied by the system in the course of time form a curve or trajectory in phase space, whose parametric equations can be written in Hamiltonian form

$$\dot{q}_i = \frac{\partial H}{\partial p_i}\,, \qquad \dot{p}_i = -\frac{\partial H}{\partial q_i} \qquad (1)$$

with the help of the Hamiltonian $H(q;p)$. The system is assumed to be conservative, i. e. $H(q;p) = E$ is a constant of the motion. In other words, the trajectory determined by the initial phase P_o is contained in the energy surface $H(P) = E = H(P_o)$ passing through P_o. We assume that all the energy surfaces of our system are contained within a finite domain of phase space : physically, this simply means that no single coordinate or momentum ever becomes infinite. This assumption therefore, is a quite natural one to make : it is fundamental for the validity of the whole ergodic theory.

It is convenient to vizualize the motion, i.e. the passage from a phase P_o to a phase P_t as a transformation of phase space into itself. The transformations $P_o \to P_t$ obviously form a continuous group, of parameter t, whose infinitesimal transformation is just given by the Hamiltonian equations (1). In other words, the motion is an automorphism of phase space. Integrals, like the Hamiltonian, are invariants of this group; the corresponding surfaces, like the energy surface, are invariant domains.

2.- Liouville's theorem. For a statistical description of a stationary state of the system, we want a measure in phase-space which is invariant for the motion group. The measure $d\mu$ introduced above has this property : this is the statement of Liouville's theorem. The most striking way of proving this theorem makes use of an anlogy between the motion in phase-space regarded as a euclidean space and a hydrodynamical of flow, whose velocity v is directly given at any point by the Hamiltonian equations (1). The theorem follows from the observation that this flo satisfies the condition of incompressibility div $\vec{v} = 0$, i.e.

$$\sum_{i=1}^{f} \left(\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} \right) = 0 \ .$$

This means in fact that any domain D_o of phase space will be transformed by the motion into a domain D_t of perhaps quite different shape, but of the same volume.

From the invariant measure $d\mu$ in the 2f-dimensional phase space it is easy to derive an invariant measure on the (2f-1) dimensional energy surface. To this end, consider an energy-shell i.e. the space between two neighbouring energy surface E, E + dE. Let $d\Sigma$ be the Euclidean measure of an element of the surface H(P) = E, and dn an element of lenght along the direction normal to the surface element $d\Sigma$. The invariant measure $d\mu_E$ on the energy surface is then :

$$d\mu_E = \frac{d\mu}{dE} = d\Sigma \cdot \frac{dn}{dE}$$

i.e. the euclidean element $d\Sigma$ is weighted with the factor dn/dE. The latter is just $|\text{grad } H(P)|^{-1} = \left\{ \sum_i \left[\left(\frac{\partial H}{\partial q_i} \right)^2 + \left(\frac{\partial H}{\partial p_i} \right)^2 \right] \right\}^{-\frac{1}{2}}$ it is numerically equal to the inverse of the modulus of the velocity $\vec{v}$ at point P. In the following, we shall always use the invariant measure $d\mu_E$, and we shall drop the index E when no confusion is to be feared.

3. Physically equivalent phases and uniform phase functions. In the preceding sections we have singled out the energy integral as

defining in 2f-dimensional space a manifold of (2f-1) dimensions which completely contains a given trajectory. It is necessary to explain the physical reason for doing so and not pursuing the reduction of the number of dimensions of this manifold any further with the help of the other time-independent integrals. For this purpose, a closer consideration of the physical interpretation of the formalism is needed.

It generally occurs that the same physical state of the system is represented by more that one phase. An example is offered by angular variables : phases in which the values of some angular variables differ by 2π describe the same physical state. Another case, of less formal character and of fundamental importance in atomistic physics, is that of systems consisting of identical elements. A phase is then defined by the sets of canonical coordinates pertaining to all the elements, enumerated in a certain order; two phases differing only by this order of enumeration are indistinguishable from the physical point of view.
To express this situation, one calls the phases as just defined specific phases, and one denotes by generic phase the set of all specific phases corresponding to the same values of all coordinates, taken in any order. A physical state of the system is thus described by a generic phase.

Phase functions representing physical quantities must have the same value for all phases corresponding to the same physical state of the system. Thus must be periodic with respect to any angular variable [+], and if they refer to a system of identical elements they must be symetrical with respect to permutations of the sets of variables pertaining to different elements. Phase functions possessing this property will be called uniform.

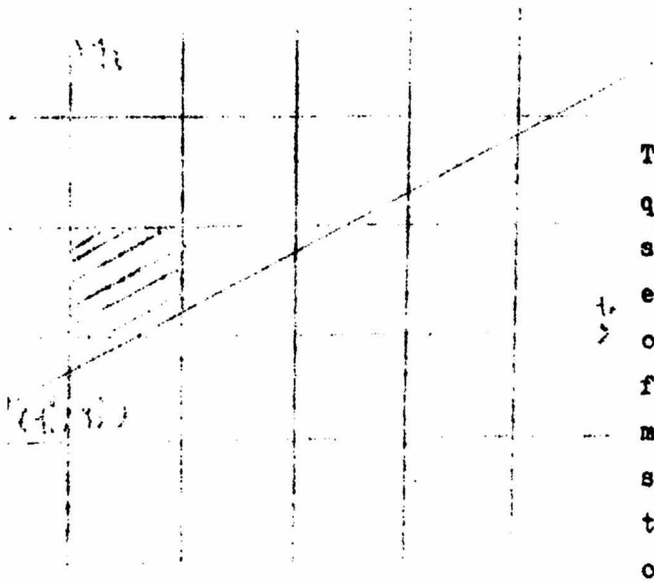
[+] Strictly speaking, angular variables do not satisfy the finiteness dondition enunciated above (§1). But they nevertheless can be used just on account of the periodicity property of all phase functions of physical significance. See the example discussed in section 4 below.

Now, if we consider a set of (2f-1) independent integrals not containing the time, which fix the shape of a trajectory, they will not in general be all uniform. We can assign the value of any uniform integral which means that we can control it by physical means; but it has no physical meaning to assign a value to a non-uniform integral. The latter can therefore in any case not be used to reduce the manifold containing the trajectory. As regards the uniform integrals, the assignment of a definite value to any one of them is purely a matter of fixing the conditions under which we wish to consider the system under investigation.

Thus, we define an isolated system by fixing the value of the energy integral. We might wish to fix the value of the momentum and angular momentum integrals : this would mean that we consider the system as free to move in empty space. In this case, the number of dimensions of the surface on which the trajectory is contained would be reduced by 6 more units. It will be more in accordance with usual conditions, however, to leave these integrals indetermined by imagining the system in contact with an infintely heavy body, with which the elements of the system interact elastically. We shall therefore base the following argument on the consideration of the energy surface; nothing essential would be changed, of course, by the assumption of a "surface" of a somewhat smaller number of dimensions, corresponding to the assignment of fixed values to other uniform integrals as well.

4.- Example. The above considerations may be illustrated by the simple example of a system of two uncoupled rotations around fixed axes. Let us take as coordinates the asimuths q_1, q_2 and assume for simplicity the two moments of inertia equal to unity; the conjugate momenta p_1, p_2, which represent the angular momenta around the axes are uniform integrals, to which we assign the values ω_1, ω_2 (numerically equal, in our case, to the angular velocities of rotation); this also fixes the energy $I = \frac{1}{2}(\omega_1^2 + \omega_2^2)$. The manifold containing the trajectory thus reduces to the plane q_1, q_2 and the trajectory is a straight line in this plane.

$q_1 = \omega_1 t + \alpha_1$, $q_2 = \omega_2 t + \alpha_2$



The plane is divided by the lines $q_1 = m.\ 2\pi$, $q_2 = n.\ 2\pi$ (m, n integers) into a chequer of squares all containing phases physically equivalent to each other. For all computation of averages of physically significant phases-functions, we may accordingly restrict the manifold containing the trajectory to a single square, by transferring to this square all the segments of the trajectory contained in the other squares. The equivalent trajectory thus obtained consists of a set of parallel segments within the single square; this set is finite or infinite according as the quantity ω_1/ω_2 is rational or irrational.

Now, we may choose as a third time-independent integral the function

$$M = q_2 p_1 - q_1 p_2 = \text{const.}$$

For the initial phase one may write $M_0 = \omega_1 q_2^0 - \omega_2 q_1^0$, but this integral is not uniform. In fact, it takes a different value on each of the finite or infinite set of segments composing the trajectory : for on the segment originally in the square containing the phase $(q_1^0 + m.\ 2\pi\ ,\ q_2^0 + n.\ 2\pi)$, the value of M differs from M_0 by $2\pi\,(n\omega_1 - m\omega_2)$.

5. Metrical indecomposability of energy surface. A question of primary importance for the establishment of a statistical distribution on the energy surface is to characterize from the metrical point of view the set of phases occupied by the system in the course of time, i. e. to know the measure of this set on the energy surface. Our simple example (§ 4) suggests that; apart from exceptionnal cases arising from some "degeneracy" (ω_1/ω_2 rational), any trajectory will in a certain sense "fill" the whole energy surface. We must try to give to this intuitive description of the physical situation a rigorous mathematical formulation.

Boltzmann and Maxwell assumed that the trajectory actually passes through every point of the energy surface : this is the famous ergodic hypothesis. It is easy, however, by the modern methods of the theory of sets, to disprove this hypothesis (Rosenthal and Plancherel). Consider a neighbourhood S of a phase occupied at some time by the system; it can be choosen sufficiently small to prevent the trajectory from remaining inside it at all times. Then it is clear that the part of the trajectory inside the neighbourhood will consist of a set of separate segments. Moreover, the time intervals during which the system is inside S will form a succession of separate finite segments of the time axis. According to a well-known property of sets of points, the set of such time intervals is enumerable. The segments of the trajectory inside S thus form an enumerable set, whose measure on the energy surface is zero.

A correct formulation of the "ergodic" situation is obtained from the consideration of the automorphism defined by the motion of the system. The set of phases through which a trajectory passes is clearly an invariant set with respect to this group, and we are concerned with its measure on the energy surface. Let us call the energy surface metrically indecomposable (and the group metrically transitive) if it cannot be expressed as the sum of two invariant sets both of positive measure. This means, then, that the set of phases forming a trajectory either is of measure zero (this is an exceptional case, such as that of a periodic motion; with a closed trajectory), or has the same measure as the whole energy surface.

At first sight, the condition of metrical indecomposability of the energy surface would seem impossible to fulfil. Let us in fact consider any time-independent integral I(P), different from the Hamiltonian; the phase-function I(P) therefore cannot have the same value over the whole energy surface. But then it is always possible to find a number I such that the invariant sets of phases for which $I(P) > I$ and $I(P) \leq I$, respectively, are both of positive measure.+ At this point it is necessary to remember that there may be

+ For the proof, see Khinchin, p. 30, footnote.

different phases corresponding to the same physical state of the system; we might then have an invariant subdivision of the energy surface into parts of positive measure, such that no two phases of any part are physically equivalent (e.g. the chequer of squares in our example, §4) such a subdivision, while formally violating the condition of metrical indecomposability as formulated above, would nevertheless represent, physically, an"ergodic"situation.

We must accordingly modify the definition of metrically indecomposable sets so as to cope with this case. We call an invariant subdivision of the energy surface into two parts of positive measure <u>essential</u> when all physically equivalent phases belong to the same part. The surface will then be <u>metrically indecomposable in the physical sense</u> when it does not allow of any essential subdivision. This modification will not affect the above argument in respect of uniform integrals : these will bring about an essential subdivision of the energy surface. But we cannot say anything about the effect of non-uniform integrals; in fact, in the example of § 4, it can be shown that the non-uniform integral M in the general case (ω_1/ω_2 irrational) does not disturb the metrical indecomposability of the (reduced) energy surface.

The next question would be, how from the structure of the Hamiltonian could one draw conclusions regarding the metrical indecomposability of the corresponding reduced manifold. This problem is not solved, however; in this sense, the assumption of the metrical indecomposability of the reduced manifold remains an hypothesis. The progress with respect to the original ergodic hypothesis lies in its precise mathematical formulation.

As we have just seen, we can only assume metrical indecomposability for the manifold reduced by taking account of <u>all</u> uniform integrals. In practice, however, the uniform integrals distinct from the energy will usually have the same value over a very large part of the energy surface, and it will be possible to neglect the domains of very small measure in which they differ from this dominant value. We may therefore still restrict ourselves to the consideration of the energy surface and speak, in this approximate sense, of its metrical

indecomposability.

6.- Poincaré's theorem. From the discussion of the "shape" of the trajectories we now pass to the consideration of the way in which they are followed by the system in the course of time. This question is dominated by a theorem enunciated by Poincaré and proved rigorously much later by Caratheodory : for almost all trajectories, the system returns after a sufficiently long time arbitrarily near to its initial phase. An essential condition for the validity of Poincaré's theorem is the finiteness of the energy surface containing the trajectories.

The proof consists in showing that the set of exceptional trajectories, i.e. the set of those phases near which the system never returns, is of measure zero. We must first formulate in a precise way what we mean by the "return" of the system near some phase P_o. Let us choose some time interval τ and consider the sequence (P) of phases P_o, P_1, P_2, ... successively occupied by the system at times t_o, $t_o+\tau$, $t_o+2\tau$, ... We shall then say that the system returns near P_o if every neighbourhood ζ_{P_o} of P_o, however small, contains at least a point of the sequence (P). The exceptional phases will thus be those for which a neighbourhood can be found containing no point of the sequence (P). We must prove that the set of exceptional phases is of measure zero.

To this end, we cover the energy surface with a net, dividing it into intervals U_i, and so fine-meshed that for every point P and every neighbourhood ζ_P of P, there is at least one interval U_k containing P and contained within ζ_P : this means that we must actually have an infinitely fine mesh, and an enumerable infinity of intervals U_i . Let now D_i be the set of phases of U_i whose time-sequence (P) never returns to U_i or its boundary; the set D_i is therefore open and accordingly measurable. Moreover, the sum $D = \sum D_i$ is the set of exceptional phases : in fact, every point of D is clearly an exceptional phase, and conversely, it will readily be seen that any exceptional phase must belong to one of the sets D_i.

Consider now one of the D_i's and the sequence of sets $D_i^{(\ell)}$, $\ell = 1,2,\ldots$ into which D_i is successively transformed at times $t_0+\tau$, $t_0+2\tau$, ... $t_0+\ell\tau$, ... No two sets of this sequence can have common points, otherwise D_i would have some phase in common with a $D_i^{(\ell)}$, i.e. there would be a point of D_i whose sequence (P) would return to D_i, in contradiction to the definition of this set. The sequence D_i, $D_i^{(1)}$ is thus an enumerable infinity of distinct sets, all of the same measure, (according to Liouville's theorem); the measure of their sum, which is the sum of their measures, must be finite, since it cannot exceed the total measure of the energy surface : therefore, the measure of each of them must be zero. From $\mu(D_i) = 0$ it follows that $\mu(D) = 0$, which we wanted to prove.

While a strictly periodic behaviour of a mechanical system would require very special conditions, Poincaré's theorem shows that in the general case the evolution of such a system still has a remarkable feature of near-periodicity. in that almost every state of the system will recur indefinitely at irregular intervals in the course of time, at any rate approximately. This approximation can be as close as one wishes, provided one waits long enough. Such a microscopic behaviour of a system, just as much as the reversibility of its motion in time, contrasts with macroscopic irreversibility. In the early period of elaboration of statistical mechanics, both features were emphasized by Boltzmann's opponents as throwing doubt on the consistency of the latter's statistical derivation of the second law of thermodynamics : the argument drawn from the microscopic reversibility was put forward by Loschmidt, while that based on Poincaré's theorem is known as Zermelo's objection. How such objections are overcome will appear in the course of the following argument.

Whether the recurrence phenomenon predicted by Poincaré's theorem can or cannot be observed depends entirely on the order of magnitude of the corresponding recurrence times. These times vary enormously according to the structure of the system and, of course, increase very rapidly with the number of degrees of freedom. We may get a rough idea of the situation by considering a simple example.

Consider a vessel containing 2N molecules of an ideal gas under normal conditions of temperature and pressure. The probability of finding an excess of molecules in one half of the vessel comprised between $\delta \cdot N$ and $(\delta + d\delta) N$ is, asymptotically,

$$\Pi(\delta)\, d\delta \simeq \frac{1}{\sqrt{\pi N}}\, e^{-\frac{(\delta N)^2}{N}}\, d\delta \cdot N$$
$$\simeq \sqrt{\frac{N}{\pi}}\, e^{-\delta^2 N}\, d\delta \ ,$$

if we assume that this inequality has arisen in the course of random fluctuations. Now, if it is the average time interval needed for the relative excess δ to change by $|d\delta|$, the probability of occurence of an excess in the interval $(\delta, \delta + d\delta)$ in the course of the temporal evolution of the system may be expressed as the fraction dt/T of the average time T between two successive occurrences of the excess δ. The ergodic theorem, as we shall see in the next chapter, allows us to equate the two probabilities just considered and in this way obtain an estimate of the recurrence time T for the excess δ:

$$T = \frac{1}{\Pi(\delta)} \left| \frac{dt}{d\delta} \right| \ ,$$

The average time variation of the excess δ is of the form

$$\delta \sim e^{-t/\tau} \ ,$$

where the relaxation time τ is determined by the mechanics of the irreversible diffusion process leading to the establishment of a uniform density. One has, therefore,

$$\frac{1}{\delta} \left| \frac{d\delta}{dt} \right| = \frac{1}{\tau} \ ,$$

and

$$T = \sqrt{\frac{\pi}{\delta^2 N}}\, e^{\delta^2 N} \cdot \tau \ .$$

If D is the diffusion coefficient, the order of magnitude of τ is related to the linear dimensions L of the volume in which the process takes place by a formula of the type

$$\tau \approx \frac{L^2}{D}$$

If the volume is of macroscopic dimensions, $L \approx 1$cm, say, one has $\tau \approx$ 1 sec and $N \approx 10^{19}$. Even an extremely small relative excess of

density, $\delta \gtrsim 10^{-6}$, would not recur spontaneously before times of the fantastic order of magnitude $T \gtrsim e^{10^7}$ sec. But if the volume is of microscopic dimensions, e.g. $L \gtrsim 10^{-5}$ cm, an excess of density of 1% will have a recurrence time of the order of 10^{-9} sec.

II. The Ergodic Theorems.

1.- Existence of the time average. Let us consider the evolution of a system starting at time t_o from a certain phase P_o. As explained in the introduction, the measurement of some macroscopic quantity corresponding to the microscopic phase function $f(P)$ yields in the first instance a time average

$$F(P_o; t_o, T) = \frac{1}{T}\int_{t_o}^{t_o+T} f(P_t)\, dt, \qquad (1)$$

taken along the trajectory defined by the initial phase P_o; in this formula, the symbol P_t denotes the set of canonical coordinates of a point of this trajectory, expressed as functions of the time and the initial conditions P_o, t_o. One is led to expect that this time of average has a limit for $T \to \infty$, which is independent of the initial conditions and represents the value of the macroscopic quantity for the system in its given stationary state. We must now discuss the mathematical justification of this surmise.

The first step is described by Birkhoff's ergodic theorem, which states that the limit

$$F(P_o) = \lim_{T\to\infty} F(P_o; t_o, T) \qquad (2)$$

exists for almost all trajectories, and is independent of the initial time t_o. We first prove the theorem for the case that the time interval T varies by finite increments of duration T, i.e. we take $T = n\tau$ and investigate the limit of the sequence

$$F_n(P_o; t_o) \equiv F(P_o; t_o, n\tau) \qquad (3)$$

as $n \to \infty$. Let P_o be an exceptional phase, i.e. such that $F_n(P_o; t_o)$ has no limit; this means that the lower bound $\underline{F}(P_o)$ and the upper bound $\overline{F}(P_o)$ are different. We can then choose a pair of members α, β ($\alpha < \beta$) between $\underline{F}(P_o)$ and $\overline{F}(P_o)$, i.e. such that

$$\underline{F}(P_o) < \alpha \qquad \overline{F}(P_o) > \beta \qquad (4)$$

Now, if the set D of exceptional phases were of positive measure, it is easily seen [1] that one could find a pair (α, β) for which the

---

[1] For details, see Khinchin, p. 19-27

conditions (4) are satisfied for all the phases P_o of a subset D^* of positive measure. By showing that this last property $\mu(D^*) > 0$ is contradictory to the inequality $\alpha < \beta$, we deduce that the set D of exceptional phases is of measure zero.

The contradiction is elicited as follows. Let us consider the sequence of times $t_k = t_o + k\tau$ and the corresponding phases $P_k = P_{t_k}$ (k being an integer of any sign), we define

$$f_k(P_o) = \frac{1}{\tau} \int_{t_k}^{t_{k+1}} f(P_t)\, dt \qquad (5)$$

the time average over the interval (t_k, t_{k+1}). By a change of origin of the times, we see that

$$f_k(P_o) = f_o(P_k) \,, \qquad (6)$$

Now, the time average $F_n(P_o; t_o)$ is expressed as

$$F_n(P_o; t_o) = \frac{1}{n} \sum_{k=0}^{n-1} f_k(P_o),$$

and if we integrate this over any set of phases $D_o^{(n)}$, we get

$$n \int_{D_o^{(n)}} F_n(P_o; t_o)\, d\mu = \sum_{k=0}^{n-1} \int_{D_o^{(n)}} f_k(P_o)\, d\mu = \sum_{k=0}^{n-1} \int_{D_k^{(n)}} f_o(P)\, d\mu,$$

where $D_k^{(n)}$ is the transform of the set $D_o^{(n)}$ when $P_o \to P_k$. If now $D_o^{(n)}$ is a subset of D^* such that for any P_o of $D_o^{(n)}$ one has $F_n(P_o; t_o) > \beta$, we obtain the inequality

$$\sum_{k=0}^{n-1} \int_{D_k^{(n)}} f_o(P)\, d\mu > n\beta\, \mu(D_o^{(n)}) \,.$$

Suppose further that the sets $D_k^{(n)}$ are non-overlapping, and call their sum

$$D^{(n)} \equiv \sum_{k=0}^{n-1} D_k^{(n)}$$

Since, by Liousville's theorem, $\mu(D_k^{(n)}) = \mu(D_o^{(n)})$, we then have

$$\int_{D^{(n)}} f_o(P)\, d\mu > \beta\, \mu(D^{(n)})$$

Now it can be shown that such sums of non-overlapping sets $D^{(n)}$ can actually be specified for each value of n in such a way that they together exhaust D^*. We can then sum the inequqlities of the type just derived for all n, and we get in the limit $n \to \infty$

$$\int_{D^*} f_o(P)\, d\mu > \beta\, \mu(D^*) \,.$$

A similar argument leads to $\int_{D^*} f_0(P)\, d\mu < \alpha\, \mu(D^*)$,

and these two inequalities with $\mu(D^*) > 0$, do indeed contradict the inequality $\alpha < \beta$.

To complete the proof of Birkhooff's theorem, we have to compare the average for an arbotrary time interval T with that for the interval of the sequence n τ nearest to T. We have

$$\left| \frac{1}{T} \int_{t_0}^{t_0+T} f(P_t)\, dt - \frac{1}{n\tau} \int_{t_0}^{t_0+T} f(P_t)\, dt \right| \to 0,$$

and

$$\left| \frac{1}{n\tau} \int_{t_0}^{t_0+T} f(P_t)\, dt - \frac{1}{n\tau} \int_{t_0}^{t_0+nT} f(P_t)\, dt \right| = \frac{1}{n\tau} \left| \int_{t_0+n\tau}^{t_0+T} f(P_t)\, dt \right| \leqslant \frac{1}{n} \left| f_n(P_0) \right|,$$

with the notation (5). It is readily verified * that

$$\lim_{n \to \infty} \frac{1}{n} \left| f_n(P_0) \right| = 0$$

almost everywhere. The proof is of the familiar type : one shows by making use of (6) and of Liouville's theorem, that the set of phases P_0 for which $|f_n(P_0)| > n\varepsilon$ is of measure zero. Hence, the time average $F(P_0; t_0, T)$ has a limit for $T \to \infty$ almost everywhere.

Finally, it must be shown that this limit is independent of the initial time t_0. We have

$$\lim \frac{1}{T} \int_{t_0}^{t_0+T} = \lim \frac{1}{T+t-t_0} \int_{t_0}^{t_1+T} = \lim \frac{1}{T} \int_{t_0}^{t_1+T}$$

since the difference of the last two expressions tends to zero like $(t_1 - t_0) / T$. Further, the difference

$$\frac{1}{T} \int_{t_0}^{t_1+T} - \frac{1}{T} \int_{t_1}^{t_1+T} = \frac{1}{T} \int_{t_0}^{t_1}$$

also tends to zero, which complete the proof.

2;- Equivalence of time average and statistical average.

The time average whose existence is established by Birkhoff's theorem does not yet correspond, in general, to the physical notion of a macroscopic quantity attached to an isolated system, since it may still depend on the particular trajectory followed by the system and have different values for different trajectories even on the same energy surface. It

is easy, however, to indicate a general condition sufficient to ensure the constancy of all time averages almost everywhere on the energy surface : it is the metrical indecomposability of this surface, at least in the physical sense. For if the time average $F(P)$ is not almost everywhere constant, it is possible to find a value F of $F(P)$ such that the conditions $F(P) > F$ and $F(P) \leqslant F$ define two invariant sets of positive measure, effecting an essential decomposition of the energy surface.

If the energy surface is metrically indecomposable, the constant value of the time average can be expressed as a statistical average over this surface. Roughly speaking, the trajectory along which the time average is taken "fills" the whole energy surface : the time average can thus be considered, if we disregard the temporal succession of the phases as an average over the energy surface, with a definite weighting of each surface element. This statistical weight turns out to have an extremely simple specification : if we use the <u>invariant measure</u> on the surface, the statistical distribution equivalent to the time average is <u>uniform</u>; in other words, the amount of time spent by the system in any region of the surface is proportional to the invariant measure of this region. This uniform statistical distribution is called <u>ergodic</u> and the fundamental corollary of Birkhoff's theorem which express this situation can be formulated as follows :

If the energy surface Ω is metrically indecomposable, the time average F of the phase function $f(P)$ is given by the ergodic average

$$\bar{f}|_E \equiv \frac{1}{\mu(\Omega)} \int_\Omega f(P)\, d\mu_E \,. \qquad (7)$$

In the first place, it is clear that the ergodic average of $f(P)$ is the same as that of the time average $F(P_0; t_0, T)$ over any finite time interval T; indeed

$$\frac{1}{\mu(\Omega)} \int_\Omega F(P_0; t_0, T)\, d\mu_E = \frac{1}{T} \int_{t_0}^{t_0+T} dt \, \frac{1}{\mu(\Omega)} \int_\Omega f(P_t)\, d\mu_E$$

$$= \frac{1}{T} \int_{t_0}^{t_0+T} dt \, \frac{1}{\mu(\Omega)} \int_\Omega f(P_0)\, d\mu_E$$

in virtue of the invariance of the energy surface Ω ; and this is

$$= \frac{1}{T}\int_{t_0}^{t_0+T} f\,dt = f\Big]_E$$

Since, owing to the constancy of F,

$$F = \frac{1}{\mu(\Omega)}\int_\Omega F\,d\mu_E,$$

it remains to prove that

$$\frac{1}{\mu(\Omega)}\int_\Omega [F - F(P_0; t_0, T)]\,d\mu_E = 0$$

This is readily [M] seen to be a consequence of the ergodic theorem $F(P_0; t_0, T) \to F$ for $T \to \infty$ for almost all P_0.

The last step established in the physical equivalence between time average and ergodic average is an obviuous extension of the preceding theorem ;

If the energy surface Ω is metrically indecomposable in the physical sense, the time average F of any uniform phase function f(P) is equal to its ergodic average :

$$F = f\Big]_E \qquad (8)$$

The equation (8) is valid for almost all phases of the energy surface. For the physical interpretation, it is therefore necessary to introduce a further averaging in order to eliminate the possibility that the initial phase would happen to be an exceptional one. Instead of starting from a well-defined initial phase, we thus assume an initial distribution of "copies" of our system over a finite domain of the energy surface. The time average F must then be averaged again over this domain ; any exceptional phases contained in it will not give any contribution to the average, and the result will again be expressed by an equation perfectly similar to (8). The replacement of an initial phase by an initial "cell" of finite (and arbitrary) size has a great importance for the physical interpretation of the theory. Before we discuss it, however, we shall proceed to an extension of the ergodic theory which first displays its full scope

3.- Hopf's ergodic theorem. The restriction of the phases to an energy surface is a strong idealisation of an isolated system. It is more realistic to allow a certain margin to the definition of the energy, i.e. to regard as possible all trajectories contained within

---

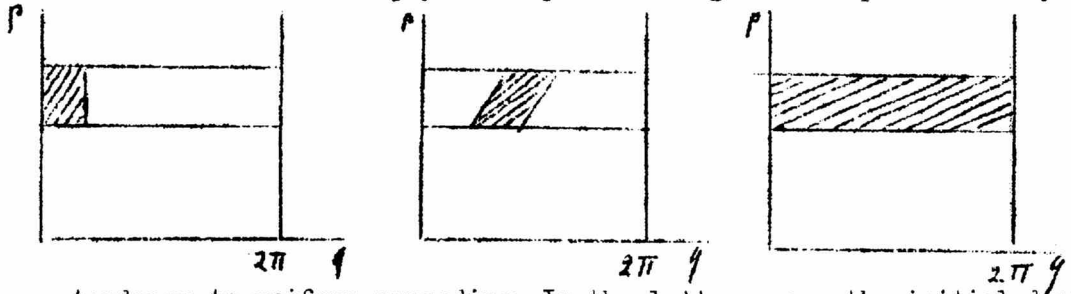
[M] See Khinchin, p. 31- 32.

an <u>energy shell</u>, consisting of all energy surfaces in the nergy interval (E, E + dE). The ergodic average over an energy shell is even somewhat simpler of expression than that on the energy surface, since it corresponds to a distribution of uniform density with respect to the simpler measure in phase-space given by Liouville's theorem : denoting the energy shell by (E) and the corresponding ergodic average by $\overline{f}\,]_{(E)}$, we have

$$\overline{f}\,]_E = \frac{1}{\mu[(E)]} \int_{(E)} f(P)\, d\mu, \qquad d\mu = dq_1 \dots dq_f\, dp_1 \dots dp_f ; \quad (9)$$

here $\mu[(E)] = \int_{(E)} d\mu$ represents the measure of the energy shell.

The condition for the equivalence of time average and ergodic average over an energy sehll is not simply that all the energy surfaces within the shell be metrically indecomposable. An additional condition is needed, involving mutual relationships between these surfaces. The situation will be made clear by a simple example. Consider a motion of a single degree of freedom, defined by an angle variable $q = \omega t \pmod{2\pi}$ and the conjugate action variable p, which is a constant of the motion. We may assume that the value of p fixes the energy; in the "phase space" (p, q,) the "energy surface" is then the line p = const., or rather the segment $0 \leqslant Q \leqslant 2$ on this line. An energy shell will be a strip limited by two such lines. While each energy line is metrically indecomposable, the situation with respect to an energy strip will be radically different according as the integral p is or is not independent of ω. In the first case, any initial distribution will simply be displaced along the strip without any



tendency to uniform spreading. In the latter case, the initial distribution, while remaining of the same total area, will spread out in the form of a more and more intricate subdivision of partial domains stretching over the whole energy strip : this illustrates the "mixing" mechanism by which the ergodic distribution is established asymptotically.

The general analysis of this "mixing" over an energy-shell has been carried out by Hopf. It introduces two new elements into the problem. In the first place, it is necessary to give a precise mathematical definition of the mixing process; morever, we must formulate the additional condition which guarantees this process to take place. The limiting process corresponding to the mixing over an energy shell is somewhat weaker than the convergence almost everywhere which obtains for the time average on an energy surface : it has the character of "convergence in the mean". To define this, let us start, at time $t_o = 0$ from some arbitrary distribution characterized by a density $g(P)$; the statistical average of a phase-function $f(P)$ for this distribution is given by

$$(f, g) = \int f(P).\, g(P)\, d\mu \ ,$$

the integration being extended to the whole phase-space (the limitation to an energy shell is contained in the form of the density function $g(P)$. At time t, the distribution density has become $g(P_t)$, i.e. the transform of $g(P)$ by the automorphism $P \rightarrow P_t$; this is some function of P and t which we denote by $\mathcal{T}_t\, g(P)$. The average of $f(P)$ at time t is accordingly $(f, \mathcal{T}_t g)$. The limiting form $\bar{g}(P)$ of the distribution density is then defined, in the sense of convergence in the mean, by the condition

$$\lim_{T \to \infty} \frac{1}{T} \int_0^T \left| (f, \mathcal{T}_t g) - (f, \bar{g}) \right|^2 dt = 0 \qquad (10)$$

for any pair of functions $f(P)$, $g(P)$. This means, physically, that the time average of the statistical fluctuations of the phase average of $f(P)$ around its limiting value $(f, \bar{g})$ tends to zero as the time T increases indefinitely. Such a formulation is all that is needed for physical applications.

We must now state the condition for the existence of a limiting distribution $\bar{g}(P)$ satisfying (10); as our example shows, this condition must express a relation between different energy surfaces : in its simplest form it must refer to a pair of energy surfaces. It is convenient, for the consideration of such a pair, to "duplicate" in a certain sense the phase space, i.e. to introduce a phase space whose coordinates consist of a pair of sets of coordinates of the original phase space : this new phase space may be described as the "direct product"

of the original one.into itself. A pair of energy surfaces of the original phase space thus appears as a single energy surface of the product space. We are now in a position to enunciate [X] Hopf's ergodic theorem : if every energy surface of the original phase space is metrically indecomposable, and almost every energy surface of the product space has the same property, every distribution tends to a limiting distribution of uniform density in the sense of equation (1o) This theorem completes the foundation of the concept of ergodic distribution, on which the whole structure of statistical thermodynamics rests.

4.- The ergodic distribution. Let us now discuss from a more physical point of view the main features of the ergodic distribution and of the mixing process by which it comes about. In considering this process we immediately face the paradox of an essentially reversible mechanism leading to an irreversible situation; but we have also in hand the means of solving this paradox. If we analyse at any instant the distirbution arising from any initial one by letting the size of the elements of phase space decrease indefinitely, we shall find that a given infinitesiaml element is either occupied or empty, and the fraction of occupied elements, by Liouville's theorem, will always remain the same : from this point of view, there is thus no mixing at all, but a perfectly reversible evolution of the distribution. If however, we fix our attention upon an element of phase space of arbitrary but finite size, the density of distribution in this element will tend asymptotically to a constant value : as Ehrenfest expressed it, the irreversible behaviour pertains to a course distribution in phase. The degree of "coarseness", i.e. the size of the cells of phase space with respect to which the distribution is defined, is arbitrary; but it is essential that some finite subdivision into cells be assumed. It is this cell-structure which represents the lack of definition of the state of the system necessary for the application of a statistical mode of description of its behaviour. From the mathematical point of view, we need not specify the size of the cells and we may even ultimately regard them as infinitesimal for the purpose of practical calcu-

---

[X] We shall not give the proof of Hopf's theorem, since it does not involve any essentially new feature.

lation; but the limiting process of letting the cell-size tend to zero must then carried out after the process of letting the time of evolution of the system tend to infinity. If we should reverse the order of the two limiting processes, we should obtain the reversible behaviour of a "fine" distribution.

The next problem concerns the time of relaxation of the mixing process, i.e. the average time which must elapse before any given distribution has pratically reached its asymptotic uniformity. At first sight, it would seen that we are landing into another paradox; our example of section 3 suggests that we must expect the mixing to proceed during a time sufficient to allow the system to return several times near phases previously occupied, in accordance with Poincaré's theorem. But the occurence of such repetitions of initial configurations is just the kind of behaviour characteristic of the purely mechanical evolution of the system as opposed to its statistical, irreversible evolution. The fantastic order of magnitude of the times of recurrence accounts for the failure to observe such repetitions in usual cases; and if the mixing process should really have to involve them, the whole statistical interpretaion of irreversibility would collapse.

To clear up the situation, it must be remembered that the usual systems to which thermodynamics is applied are composed of a large number of identical elements : they are either bodies built up of atoms or radiation fields consisting of proper oscillations. The physical states of such systems are represented by generic phases; the latter do not correspond to single "cells" of phase space but to regions called "constellations" by Ehrenfest containing many cells and intrically imbricated through each other over each energy shell. The measure of a constellation, according to the ergodic theorems, gives the relative probability of occurence of the state represented by the corresponding generic phase in the course of time. States very near to equilibriul will thus occuoy a much larger part of the energy shell than states deviating appreciably from the equilibrium conditions. Thus, if a trajectory starts from such an "improbable" constellation, it will soon enter into more and more porbable ones and when it will have reached the equilibriul consteallation, it will stay in it most of the time , although it will continually cross less probably ones, appearing as "fluctuations"

from the equilibrium state. The return of a very improbable state, i.e. the return of the trajectory to a very improbable constellation, would require a time of a fantastic order of magnitude; but the time of relaxation is defined as that needed to reach the most probable constellation, starting from a less probable one; and this is extremely short as soon as the number of elements is reasonably large. The importance of the consideration of generic phases for the consistency of the statistical theory in all cases in which its application is significant was, of course, fully recognized both by Gibbs and by Boltzmann. But the mode of exposition adopted by Gibbs tended to obscure this issue. Gibbs was worried by the discrepancies between theory and experiment, especially with respect to the consequences of the equipartition of energy for the specific heats; these discrepancies seemed to be connected with the assignment of the number of degrees of freedom of the atomic systems; in the hope of throwing light on the origin of the difficulty, he accordingly set himself the task to derive as rigorously as possible all those statistical properties which apply to the most general mechanical systems, without any restriction as to the number of degrees of freedom. Hence the emphasis in his book upon the derivation of such results, while the discussion of systems of identical elements was confined to the last chapter. Boltzmann strongly objected to the tendency of Gibbs' book :"I can understand statistics applied to a gas, he said,[1] but I see no point in applyingit to a sewing machine". Gibbs' distrust of detailed atomic models was part of an attitude of mind shared by many physicists towards the end of the XIXth century : it was an essentially idealistic reaction against the mechanistics school which had flourished during the second half of the century, and of which Kelvin is the typical representative. Boltzmann remained to the last a staunch supporter of the mechanistic ideal; and in spite of the fact that this ideal has now been recongized to be too narrow, it did at the time give Boltzmann the right inspiration. His views on statistical mechanics were perfectly clear and precise, although he lacked the mathematics, we now have for their appropriate expression. Yet he had to face widespread scepticism and opposition and did not live to see the triumph of his ideas.

---

[1] This utterance was reported in conversation by Ehrenfest who had been a pupil of Boltzmann's.

In fact, the objections raised against Boltzmann's position are only interesting insofar as they show the kind of misunderstanding of the significance of the statistical approach one might fall into. Loschmidt observes that if at a certain time all velocities (and magnetic fields) of the system are inverted, the system will so to speak, retrace its steps : if, therefore, its evolution went from less to more probable configurations, it will now exhibit an opposite trend. Zermelo, availing himself of Poincaré's theorem, pointed out that any configuration, however improbable, must be expected to repeat itself with arbitrary accuracy in the course of the time. Both assertions are, of course, perfectly true : they can be vizualized by following the path of the system among the enfilement of the various constellations. But they are beside the point : it is the course distribution which has an irreversible evolution, and we have seen that such an irreversible trend is perfectly compatible with the reversibility of the mechanism by by the "mixing" of the course distribution is brought about.

5. - Systems with weak interactions. We may follow up the last argument more quantitavely. We introduce the phase space of a single element of the system, the "μ-space" in Ehrenfest's terminology. The total phase space of a system of N elements, or "Γ-space", is the direct product of N identical μ-spaces. Let us subdivide the μ-space into cells of arbitrarily small, but finite size ω_i ; this defines a subdivision of Γ-space into cells corresponding to the specific phases of the system. Thus, consider the specific phases for which there are N_i elements in the μ-cell ω_i : they occupy a cell in Γ-space of measure $\omega_1^{N_1}\omega_2^{N_2}\cdots$, or $\prod_i \omega_i^{N_i}$. To find the measure of the corresponding generic phase, we have simply to multiply this by the number of ways in which the N elements can be arranged in groups of N_1, N_2,....., i.e. $N!\ /\ N_1!\ N_2!\ \ldots$; the measure of the generic phase is thus

$$\Omega(N_1, N_2, \ldots) = N! \prod_i \frac{\omega_i^{N_i}}{N_i!}$$

To go on with explicit calculations, we must restrict ourselves to a particular type of system : we assume that the interactions between its elements can be neglected ; examples of such systems are the ideal gas and the pure radiation field. It is important to note that in order for the equilibrium distribution of the system to be ergodic, it is essential that the elements do interact ; otherwise, the numbers of elements in the various energy shells of μ-space would obviously remain unaltered in the course of time.

But the magnitude of the interaction is irrelevant

and in suitable circumstances can be ragarded as negligible in comparison with the proper energies of the elements. In this case, we may assign a well-defined energy E_i to all elements in the μ-cell ω_i and the total energy of the system is an additive function of the E_i's :

$$E = \sum_i N_i E_i \tag{12}$$

If the total energy E is given, this is a condition imposed on the distribution of the elements among the cells ω_i. Another condition is, of course

$$N = \sum_i N_i \tag{13}$$

We may now readily evaluate the distribution N_i which, under the conditions (12) (13) gives the constellation of maximum measure (11). If the N_i's are large, the asymptotic expression for this distribution is

$$\overline{N_i}\Big|_E \simeq \frac{N}{Z}\,\omega_i\, e^{-\beta E_i} \tag{14}$$

where

$$Z \equiv \sum_i \omega_i\, e^{-\beta E_i} \tag{15}$$

and the parameter β must be determined in terms of E from the condition (12). In evaluation, the "sum over states" Z it is permissible to treat the μ-cells as infinitesimal, and to write

$$Z = \int e^{-\beta H(p,q)}\, d\mu\,, \tag{16}$$

where $H(p,q)$ is the Hamiltonian of a single element and the integration is extended to the whole μ-space.

Let us now evaluate the measure $\Omega\left(\overline{N_1}\Big|_E, \overline{N_2}\Big|_E, \dots\right)$ of the equilibrium constellation, and compare it with the measure of the energy shell in Γ space in which it is contained. We have

$$\log \Omega\left(\overline{N_1}\Big|_E, \overline{N_2}\Big|_E, \dots\right) \simeq N \log Z + \beta E\,, \tag{17}$$

so that the problem is reduced to the computation of $\log Z$. To this end, we decompose the integration in μ space into an integration over all the values of the energy and another over each energy surface in turn, using, of course, the invariant measure in accordance with $d\mu = d\mu_E \cdot dE$. For the invariant measure of the energy surface E we write

$$\mu(E) = e^{\sigma(E)}\,;$$

thus

$$Z = \int_{-\infty}^{+\infty} e^{\sigma(E) - \beta E}\, dE$$

The exponent of the integrand has a maximum for an energy E_m given by

$$\left(\frac{d\sigma}{dE}\right)_m = \beta$$

Expanding it near the maximum, we have, to a sufficient approximation,

$$\sigma(E) - \beta E = \sigma(E_m) - \beta E_m + \frac{1}{2}\left(\frac{d^2\sigma}{dE^2}\right)_m (E - E_m)^2 ;$$

the coefficient $\frac{1}{2}\,(d^2\sigma / dE^2)_m$ is assumed to be negative. This defines a Gaussian distribution of the energy around the extremal values E_m. The mean square fluctuation $\overline{\Delta E^2}$ of the energy is $\left|(d^2\sigma / dE^2)_m\right|^{-1}$, which gives the physical meaning of the latter qhantity. To this approximation, we get for $\log Z$

$$\log Z \approx \log \mu(E_m) - \beta E_m + \log \sqrt{2\pi\,\overline{\Delta E^2}}$$

$$\approx \log \mu\left([E_m]\right) - \beta E_m ,$$

if we denote by $[E_m]$ an energy shell in μ-space of thickness $\sqrt{2\pi\,\overline{\Delta E^2}}$ around the energy surface E_m. Inserting the last formula into (17) and noting that $NE_m \approx E$, we see that $\Omega\left([N_1]_E, [N_2]_E, \ldots\right)$ takes the form $\mu\left([E_m]\right)^N$ of the measure of the energy shell in Γ space consisting of the shells $[E_m]$ in all the μ-spaces. In this sense, we may say that, asymptotically, the equilibrium constellation is equivalent to the whole energy shell in Γ space. The distribution (11), which completely describes the equilibrium constellation, may therefore be used to compute, to a sufficient approximation, the ergodic averages of all additive phase functions for the special type of system here considered and, in particular, to define the thermodynamical functions pertaining to it. We shall come back to this last point in a moment, after having discussed it for the most general isolated systems.

6.- Thermodynamics of isolated systems. Isolated systems do not lend themselves very well to a discussion of thermal quantities, for the definition of temperature requires, from the physical point of view, the possibility of an exchange of energy between the system and its surroundings. Nevertheless, one can speak of the entropy of an isolated system and may thus ask for the atomistic interpretation of this quantity. The temperature will thus not receive any direct physical interpretation, but will appear as a derived concept. We shall give later a more satisfactory treatment of this problem; but we may just as well take it up at this stage in order to present the general point of view from which it is considered.

Let us first recall the peculiar way in which macroscopic variables enter into the fundamental thermodynamics relations. Each non-thermal physical aspect is represented by a pair of variables (a, A) whose

mutual

relationship is characterized by saying that if the magnitude of a is controlled by some agency external to the system, the work done on the system to change a by da is Ada. In the atomistic treatment, we may take account of these macroscopic variables (a, A) by introducing into the Hamiltonian of our sysyem suitable terms of potential energy which will contain the parameters a. The associated variables A, called "forces" in an extended sense, will then be defined as the statistical averages of the phase functions $(\partial/\partial a) H(p,q;a)$. For an isolated system, we must take the ergodic averages :

$$A = \overline{\frac{\partial H}{\partial a}}\Big|_E$$

The thermal transformations are also formally represented by a pair of associated variables, the entropy and the temperature, but these must, of course, be treated separately and in a quite different way.

For an isolated system, the independent variables (i.e. those which are controlled by external agencies) are the energy E and the parameters a. The entropy then plays the part of the characteristic function, from which all other quantities are obtained by differentiation and algebraic cpmbination. If θ denotes the absolute temperature, one has

$$d S = \frac{1}{\theta} dE - \frac{A}{\theta} da, \qquad (18)$$

so that

$$\frac{1}{\theta} = \left(\frac{\partial S}{\partial E}\right)_a , \quad - \frac{A}{\theta} = \left(\frac{\partial S}{\partial a}\right)_E . \qquad (19)$$

We shall always give the temperature, the dimension of an energy; the entropy will accordingly be dimensionless. Now, we can readily indicate an expression pertaining to the atomistic description of the system and which formally satisfies the relations (19) characteristic of the entropy. Let Ω represent the part of phase space "enclosed" by the energy surface E, i.e. containing all the energy surfaces corresponding to energy values $\leq$ E. We may then take

$$S = \log \mu(\Omega) \qquad (20)$$

The verification of the suitability of this definition must be limited to the second relation (19), since the first one can only be regarded as a formal definition of the temperature. In order to calculate the derivative $\partial S/\partial a$ at constant E, let us introduce the characteristic set function $\chi(\Omega)$ of the set Ω , i.e. a function equal to unity for all

phases of Ω and zero for all other phases; in the present case, we may express $\zeta(\Omega)$ very simply as the "step" function $\zeta(x)$ of the argument $x = E - H(p,q,a)$:

$$\zeta(x) = \begin{cases} 1 & \text{for } x \geqslant 0 \\ 0 & \text{for } x < 0 \end{cases}$$

The derivative of $\zeta(x)$ is the distribution $\delta(x)$. This allows us to write

$$\mu(\Omega) = \int \zeta\left[\bar{E} - H(p,q;a)\right] d\mu$$

the integration extending to the whole phase space. We further get

$$\frac{\partial \mu(\Omega)}{\partial a} = -\int \frac{\partial H}{\partial a}\, \delta\left[\bar{E} - H(p,q;a)\right] d\mu$$

$$= -\int dE' \delta(E-E') \int_{E'} \frac{\partial H}{\partial a}\, d\mu_{E'} = -\int \frac{\partial H}{\partial a}\, d\mu_E = -\left.\frac{\partial \bar{H}}{\partial a}\right|_{H(E)}$$

Therefore $$\frac{\partial \log \mu(\Omega)}{\partial a} = -A \cdot \frac{\mu(E)}{\mu(\Omega)}$$

But clearly $$\mu(\bar{E}) = \frac{\partial \mu(\Omega)}{\partial E},$$

and therefore $$\frac{\mu(E)}{\mu(\Omega)} = \frac{\partial \log \mu(\Omega)}{\partial E} = \frac{1}{\theta}$$

whence finally $$\frac{\partial \log \mu(\Omega)}{\partial a} = -\frac{A}{\theta}$$

In the special case of systems with weak interactions, discussed in the preceding section, we may, of course, use the definition (20) of the entropy; but we may just as well take for this purpose a somewhat different definition, viz.

$$\zeta = \log \Omega\left(\bar{N}_1|_E, \bar{N}_2|_E, \ldots\right), \qquad (21)$$

whose explicit form is given by (17). The "force" A is now expressed as an average over the most probable distribution (14)

$$A = \frac{N}{Z} \int \frac{\partial H}{\partial a}\, e^{-\beta H}\, d\mu,$$

the Hamiltonian H(p,q;a) now referring to a single element, and the integration being extended to the corresponding μ-space. From (21) and (17) we derive

$$\left(\frac{\partial \zeta}{\partial E}\right)_a = \beta$$

which gives the interpretation of the parameter β as the inverse of the absolute temperature, and

$$\left(\frac{\partial S}{\partial a}\right)_E = -\beta \frac{N}{Z} \int \frac{\partial H}{\partial a} e^{-\beta H} d\mu = -\beta A,$$

which shows that the definition (21) of S is as acceptable as (20). It is essential for this equivalence that the system considered has a large number of degrees of freedom; for the equation (17) is an asymptotic one. This ambiguity in the entropy definition for large systems was discussed in detail by Gibbs, and also from a more physical point of view by Lorentz, who called it the "insensibility" of the entropy definition. The reason for this latitude in the choice of the function S is clear. We have seen already that the measure of $\Omega(N_1 l_2, N_1 l_2)$ is pratically the same as that of an energy shell in Γ -space; and the latter is not significantly different from the measure of the whole domain Ω when the number N of elements is very large. To give a simple example, consider an ideal monoatomic gas, whose Hamiltonian consists of the kinetic energy of translation $\frac{1}{2m}\sum_{i=1}^{3N} p_i^2$ (m being the mass of an atom) and of a potential energy expressing that the system is confined to a volume V. In computing $\mu(\Omega)$ the integrations over the position and momentum coordinates can be performed separately, the former gives a factor V^N, the latter the volume of a 3N-dimensional sphere of radius $\sqrt{2m E}$, which is proportional to $E^{(3N/2)}$. The measure $\mu(E)\Delta E$ of an energy shells differs from $\mu(\Omega)$ only by the replacement of $E^{(3N/2)}$ by $(3N/2)\, E^{\frac{3(N-1)}{2}} \Delta E$, which for very large N is quite insensible.

Our two definitions of the entropy have a common feature : they both express the entropy as the logarithm of the measure of a domain of phase space, i.e. of the relative probability of occurence, in the course of time, of the phases contained in this domain. The logarithmic character of the link between entropy and probability is easy to understand : if we unite two independent isolated systems into a single system, their entropies should be added, the probabilities of their configurations multiplied. The definition (21), usually adopted for systems with weak interactions, corresponds to a more detailed discrimination of the configurations than the general definition (20).

The law of increase of entropy appears as a statistical law. If (by removing constraints) we allow the isolated system to pass from an initial state of equilibrium to the state of equilibrium corresponding to the new conditions , the values of the entropy in the final state will

necessary be larger than the initial one ; but the behaviour of the statistical function $\log. \Omega(N_1, N_2....)$ during the transition will, as already stated, exhibit continual fluctuations (even after the new state of equilibrium is reached). The concept of entropy, however, essentially refers to the state of equilibrium under neglect of such fluctuations. The statistical interpretation thus indicates the limit of validity of the entropy concept : if the fluctuations form a prominent feature of the phenomenon, as in Brownian motion, the thermodynamical concepts become meaninglesss. The second law is not "violated", it ceases to be applicable. On the other hand, the statistical treatment is still perfectly adapted to this kind of phenomena; e.g. it can be used to evaluate the average amplitude of the observed fluctuations. In this sense, the scope of statistical mechanics is wider than that phenomenological thermodynamics.

III. Statistics of Closed Systems.

1.- System of given temperature. To ensure that a system S has a definite temperature, we must imagine it in "thermal contact" with a "thermostat", i.e. some other system T whose heat capacity is so large that the exchange of heat with the system S does not sensibly alter its temperature. The two systems S and T, freely exchanging energy with each other, have then a common temperature, which is entirely fixed by the thermostat. From the atomistic point of view, we have a total system $\mathcal{S}$ consisting of the system S under investigation and the thermostat T, such that the number of degrees of freedom of S is much smaller than that of T. While the energy of both S and T continually varies, we may assume that the total energy of $\mathcal{S}$ remains constant, i. e. that $\mathcal{S}$ is isolated. The problem is thus to derive from the statistical distribution of the isolated system $\mathcal{S}$ that of a small part S of $\mathcal{S}$.

For this purpose, we consider the phase-spaces of S and T, with measures $d\mu_S$, $d\mu_T$ and the product space of $\mathcal{S}$ with measure $d\mu = d\mu_S d\mu_T$. Moreover, although the systems S and T are essentially interacting, we may assume that the magnitude of the interaction is negligible, so that the total energy E is composed additively of the energies E_S, E_T of the systems S and T. We again introduce in the S- and T- spaces and in the product spaces the domains Ω_S, Ω_T, Ω enclosed by the energy surfaces E_T, E_S, E. Now, we are interested in the averages of phase functions pertaining to the system S, i.e. depending only on the phase coordinates P_S. We may write down these averages immediatly as ergodic averages in the total $\mathcal{S}$-space; we shall then seek to transform these expressions so as to eliminate the irrelevant phase coordinates P_T the thermostat will be represented in the final result by only one parameter, which play the part of the temperature.

For the transformation we have in view, it will be convenient to write the ergodic average in the form

$$\overline{f}_E = \frac{1}{\mu(E)} \frac{d}{dE} \int_\Omega f(P)\, d\mu \qquad (1)$$

For a phase function $f(P_S)$ belonging to S we may carry out the integration with respect to the variables P_T; for each phase P_S, to which corresponds an energy $E_S = H_S(P_S)$, and accordingly an energy $E_T = E - H_S$, this gives a

a factor $\mu_T[\Omega_T(E - H_S)]$. The integration over P_S extends over the domain enclosed by the surfaces corresponding to the largest value of E_S, viz. E; but we may actually extend it over the whole S - space since for larger values of E_S, the factor μ_T vanishes. Thus,

$$\int f(P_S)\, d\mu = \int f(P_S)\, \mu_T[\Omega_T(E - H_S)]\, d\mu_S .$$

The derivation with respect to E transforms $\mu_T(\Omega_T)$ into the invariant measure of the limiting energy surface $\mu_T(E - H_S)$ and we get from (1)

$$\overline{f(P_S)}\Big]_E = \int f(P_S)\, \frac{\mu_T(E - H_S)}{\mu(E)}\, d\mu_S \qquad (2)$$

We have now expressed the ergodic average of $f(P_S)$ as an average over the phase space of the system S alone, each element of this space being affected with the statistical weight $\mu_T(E - H_S)/\mu(E)$; since this weight factor only depends on the energy H_S, one may say that it affects the energy surfaces or energy shells in S - space. As a result of the contact with the thermostat, the energy E_S of the system S is not fixed, but has the equilibrium distribution given by $\mu_T(E - E_S)/\mu(E)$: we must therefore take all ergodic averages $\overline{f}\Big]_{E_S}$ and add them up with the weights corresponding to the distribution of E_S.

2.- Canonical distribution. Our next task is to find a simpler expression for the energy distribution in S - space. This means essentially that we want to transform the factor $\mu_T(E_T)$, for the factor $\mu(E)$ is easily evaluated in terms of it; in fact, by an argument similar to the above, we find

$$\mu(E) = \int dE_S\, \mu_S(E_S)\, \mu_T(E - E_S) \qquad (3)$$

the integration extending over all values of the energy E_S

Now, we note that the structure of the thermostat is entirely arbitrary, apart from the requirement that it be a very large system. We avail ourselves of this latitude to obtain an asymptotic expression for $\mu_T(E_T)$: to this end, we assume the thermostat to consist of a large number of parts T_1, T_2,... whose interactions we may neglect. By making repeated use of a formula of the type (3), we get

$$\mu_T(E_T) = \int dE_{T_1} \int dE_{T_2} \cdots \int dE_{T_{n-1}}\, \mu_{T_1}(E_{T_1})\, \mu_{T_2}(E_{T_2}) \cdots \mu_{T_n}(E_T - E_{T_1} - E_{T_2} - \cdots - E_{T_{n-1}})$$

The formal analogy of this equation with the "law of composition" of probabilities suggested to Khinchin an elegant application to our problem of the "central limit theorem" of the theory of probability.

Consider n stochastic variables $x_1, x_2, \ldots x_n$ with independent distributions $u_1(x_1)dx_1$, $u_2(x_2)dx_2, \ldots$ The distribution of the sum $x = x_1 + x_2 \pm x_n$ obeys the law of composition.

(4) $$u(x)\,dx = \int dx_1 \int dx_2 \cdots \int dx_{n-1}\; u_1(x_1)\,u_2(x_2)\cdots u_n\left(\ldots x - x_1 - x_2 - x_n\right)$$

Now, provided that the distribution laws $u_i(x_i)$ satisfy certain conditions the most important being that the mean fluctuations of the variable x_i are finite, the distribution law for x has the asymptotic form (for $n \to \infty$

$$u(x)\,dx \simeq \frac{1}{\sqrt{2\pi B}}\; e^{-\frac{(x-\bar{x})^2}{2B}} \qquad (5)$$

where $\bar{x} = \sum_n \bar{x}_n$ is the sum of the average values $\bar{x}_i = \int x_i\, u_i(x_i)\, dx_i$, i.e. the average value of x, and $B = \sum_n \beta_n$ is the sum of the mean quadratic fluctuations

$$\beta_i = \int (x_i - a_i)^2\, u_i(x_i)\, dx_i$$

We cannot, however, immediately identify $\mu_{T_i}(E_{T_i})\, dE_{T_i}$ with a distribution law $u_i(x_i)dx_i$ because the measures $\mu_{T_i}(E_{T_i})$, though finite, are not necessarily bounded : they generally increase as some power of the energy. This obstacle is, of course, easily overcome by putting

$$u_i(E_{T_i}) = \frac{1}{Z_i(\beta)}\; e^{-\beta E_{T_i}}\, \mu_{T_i}(E_{T_i}) \qquad (6)$$

where

$$Z_i(\beta) = \int e^{-\beta E_{T_i}}\, \mu_{T_i}(E_{T_i})\, dE_{T_i} \qquad (7)$$

secures the normalization, and β is an arbitrary positive parameter. In fact, the u_i's so defined are bounded and satisfy the law of composition (4); it can be verified in detail + that they satisfy all the conditions for the validity of the asymptotic formula (5).

The law of distribution $u(E_T)$ derived from the set (6) by the law of composition (4) has exactly the same form as each of the u_i's, the normalization factor $Z(\beta)$ being the product of the Z_i's. We readily get

$$\bar{E}_T = -\frac{d \log Z}{d\beta} \qquad (8)$$

and

$$B_T = \frac{d^2 \log Z}{d\beta^2} \qquad (9)$$

+ Voir Khinchin, p. 86

It is easily seen [+] that equation (8) umiquely determines β in terms of $\overline{E}_t$: this makes it possible to fix the parameter β by relating it to the given average energy of the thermostat. We shall henceforth assume that β has the value resulting from this equation (8) : it is this parameter which will "represent" the thermostat in the final result, and we shall see that it is simply related to the temperature.

Taking for $\mu(E_T)$ its asymptotic form (7) we get for $\mu_T(E_T)$ the asymptotic expression

$$\mu_T(E_T) \simeq \frac{Z_T(\beta)}{\sqrt{\quad}} \; e^{\beta E_T - \frac{(E_T - \overline{E}_T)^2}{2 B_T}} \qquad -(10)$$

In applying this formula to the argument $E_T = E - E_S$, we note that $(E_T - \overline{E}_T)^2 = (E_S - \overline{E}_S)^2$. Now, excepting the unliky cases when E_S happens to be widely different from its average $\overline{E}_S$, the quadratic fluc- tuations of the system S will be of a much smaller order of magnitude that those of the thermostat whose average is given by B_T : we shall accordingly neglect them altogether and write

$$\mu_T(E - E_S) \simeq \frac{Z_T(\beta)}{\sqrt{2\pi B_T}} \; e^{\beta(E - E_S)}$$

For the factor $\mu(E)$ we may write down a completely similar expression since according to (3) the systems S and T are linked together by the same law of composition as the various parts of T : we may therefore treat the total system S as we have just treated the thermostat. Thus,

$$\mu(E) \simeq \frac{Z(\beta)}{\sqrt{2\pi B}} \; e^{\beta E}$$

and

$$Z(\beta) = Z_T(\beta) \; Z_S(\beta)$$

while B differs from B_T only by the contribution from the small system S which can be neglected. For the energy distribution of the system S we therefore get the very simple expression

$$\frac{\mu_T(E - E_S)}{\mu(E)} \simeq \frac{1}{Z_S(\beta)} \; e^{-\beta E_S} \qquad (11)$$

in which the thermostat only appears through the parameter β.

In its most general aspect, the property expressed by

[+] Voir Khinchin, p. 77

formula (11) may be stated as follows : any small[+] part of a large system, whose interaction with the system is weak, is distributed in energy according to the law (11). In this form, the theorem is due to Boltzmann, who recognized its fundamental importance for the statistics of non-isolated systems. The law of distribution (11), under the name of canonical distribution law, was extensively studied by Gibbs; the insufficient emphasis put by Gibbs on Boltzmann's theorem is no doubt responsible for the wisdespread confusion about the physical significance of the canonical distribution. The above derivation, due to Khinchin, has the merit of elucidating the deep-lying relation of Boltzmann's theorem to the general principles of statistics.

+ It need hardly be emphasized that the "small" part can be any macroscopic system; it is small only with respect to its surroundings, which constitute the "thermostat". On the other hand, the small part could also be just an atom of an ideal gas : Boltzmann's theorem then gives an independent derivation of the theory of systems of weakly coupled identical elements of Ch II, § 5.

3. - Energy distribution . The canonical distribution law has important consequences for the average value of the energy. In the first place, the study of this quantity will allow us to establish a very simple relation between the thermostat parameter β and the absolute temperature as usually difined. Further, we shall derive a general property known as "equipartition of the energy". Finally, it is also possible, at least for a certain class of systems, to derive the explicit law of distribution of the energy around the mean and, in particular, the mean quadratic fluctuation of the energy.

The canonical average of the energy of our system S is given by :

$$\bar{E}_S = - \frac{d \log Z_S}{d\beta}$$

If, in particular, the system S is an ideal monoatomic gas, we have (cf. Ch. 11, §6)

$$\mu(E_S) \sim E_S^{\frac{3N}{2}-1}$$

whence

$$Z_S(\beta) = \int e^{-\beta E_S} \mu(E_S)\, dE_S \sim \int e^{-\beta x} x^{\frac{3N}{2}-1} dx \sim \beta^{-\frac{3N}{2}}$$

and

$$\bar{E}_S = \frac{3N}{2} \frac{1}{\beta} . \tag{12}$$

The thermodynamical value of the energy of such a gas is $\frac{3}{2} R T$ per mole, where R is the gas constant and T the absolute temperature in the Kelvin scale. This may be written $\frac{3}{2} N\theta$, if N is the number of atoms per mole and $\theta = k T$, with $k = R/N$, is the measure of the absolute temperature in an energy scale. The conversion factor k is a universal constant to which the name of Boltzmann has been linked (although Boltzmann himself did not introduce it explicitely). The comparison with the statistical formula fixes the relation of the thermostat parameter β with the absolute temperature :

$$\beta = \frac{1}{\theta} \tag{13}$$

The simple formula (12) is a special case of a more general property. If we can isolate in the Hamiltonian of the system any group of terms H' homogeneous and quadratic in some of the p's, i.e. such that :

$$H' = \frac{1}{2} \sum_{i=1}^{k} p_i \frac{\partial H'}{\partial p_i}$$

we may perform the calculation of the canonical average $\bar{H}'$ explicitly. In fact, putting $H = H' + H''$, we may write :

$$\bar{H}' = \frac{1}{Z} \int d\mu'' e^{-\beta H''} \int H' e^{-\beta H'} d\mu' ,$$

where $d\mu = d\mu' d\mu''$ with $d\mu' = dp_1 \dots dp_k$. Now, for any of the relevant p_i's we have

$$\int p \frac{\partial H'}{\partial p} e^{-\beta H'} dp = -\frac{1}{\beta} \int p \frac{\partial}{\partial p} \left(e^{-\beta H'} \right) dp = +\frac{1}{\beta} \int e^{-\beta H'} dp$$

whence

$$\bar{H}' = \frac{k}{2} \frac{1}{\beta} = k \cdot \frac{1}{2} \theta . \qquad (14)$$

The same argument applies to the case that the quadratic homogeneous part of the Hamiltonian belongs to the potential energy, i.e. has this property with respect to some of the q's.

The general formula (14) expresses the law of equipartition of the energy : for a system of temperature θ, every degree of freedom for which the kinetic or potential part of Hamiltonian is homonogeneous and quadratic in the corresponding canonical variable contributes $\frac{1}{2} \theta$ to the average energy of the system. In particular, every degree of freedom of harmonic oscillation contributes θ to the average energy.

If the system S can itself be analysed into a large number of component parts with weak interactions, e.g. if it is an ideal gas, we can apply to the measure of its own energy surfaces $\mu_S (E_S)$ the asymptotic formula that we had derived for the thermostat. The law of distribution of the values E_S of the energy then takes the simple form :

$$w(E_S) = \mu_S(E_S) \frac{\mu_T(E - E_S)}{\mu(E)} = \frac{Z_S(\beta)}{\sqrt{2\pi B_S}} e^{\beta \bar{E}_S - \frac{(E_S - \bar{E}_S)^2}{2B_S}} \cdot Z_T(\beta) e^{\beta(E - E_S) - \frac{(\bar{E}_S - \bar{E}_S)^2}{2B_T}} \cdot \frac{\sqrt{2\pi B}}{Z(\beta)} e^{-\beta E}$$

$$= \frac{1}{\sqrt{2\pi B_S^*}} e^{-\frac{(E_S - \bar{E}_S)^2}{2B_S^*}} ,$$

where B_S is defined by

$$\frac{I}{B_S^*} = \frac{I}{B_S} + \frac{I}{B_t} = \frac{B}{B_S B_t}$$

We thus obtain a Gaussian distribution of the energy with a mean quadratic fluctuation B_S^* which is always smaller than B_S : the exchange of energy with the thermostat thus results in a negative correlation of the energy distribution between the two parts of the total system.

The value of the mean quadratic fluctuation B_S is easily computed. One has

$$B_S = (E_S - \bar{E}_S)^2 = \overline{E_S^2} - (\bar{E}_S)^2$$

$$\bar{E}_S = \frac{-d \log Z}{d\beta}, \qquad \overline{E_S^2} = + \frac{1}{Z} \frac{d^2 Z}{d\beta^2}, \qquad \frac{d\bar{E}_S}{d\beta} = - \frac{1}{2} \frac{d^2 Z}{d\beta^2} + \frac{1}{Z^2} \left(\frac{dZ}{d\beta} \right)^2$$

i. e.

$$B_S = - \frac{d \bar{E}_S}{d\beta} = \frac{d \bar{E}_S}{d\theta} \theta^2 \qquad (15)$$

This formula exhibits a fundamental feature common to all fluctuation phenomena : while the product $\theta \frac{d\bar{E}_S}{d\theta}$ is of macroscopic order of magnitude, there is an extra factor θ which contains the essentially atomistic constant k. In fact, fluctuation phenomena are outside the scope of macroscopic physics : they are essentially linked to the atomic theory of matter and radiation. Accordingly, the observation of their macroscopic effects, such as Brownian motion, light scattering, etc., affords a proof of the consistency of the atomic picture and a possibility of determination of atomic dimensions.

4.- Thermodynamics of closed systems. We shall now follow a line of argument parallel to that developped for isolated systems. We shall look for an atomistic interpretation of the characteristic function corresponding to the choice of the temperature and the extremal parameters as independent variables : this is the free energy of the system, defined as[+]:

$$F = \bar{E} - \theta S \qquad (16)$$

In fact, we find

$$dF = - S \, d\theta + A \, da, \qquad (17)$$

i.e.

$$S = - \left(\frac{\partial F}{\partial \theta} \right)_a, \qquad A = + \left(\frac{\partial F}{\partial a} \right)_\theta \qquad (18)$$

From (16) and (17), we derive, by making use of the general transforma-

---

[+] We may now drop the index

tion formula : $\theta \frac{\partial \rho}{\partial \theta} = -\beta \frac{\partial f}{\partial \beta}$,

the Helmholtz relation between mean energy and free energy

$$\bar{E} = F - \theta \frac{\partial F}{\partial \theta} = \frac{\partial}{\partial \beta}(\beta F) \qquad (19)$$

Now, a direct calculation gives for the canonical average of the force $(\partial H / \partial a)$

$$A = -\frac{1}{\beta} \frac{\partial \log Z}{\partial a} \quad ;$$

this formula, together with the previous one

$$\bar{E} = -\frac{\partial \log Z}{\partial \beta} \quad ,$$

shows by comparison with the second equation (18) and with (19), respectively, that we must take for F the expression

$$F = -\theta \log Z \quad , \qquad (20)$$

except for an arbitrary linear function of θ (without physical meaning) Formula (20) completes the atomistic interpretation of the thermal quantities pertaining to closed systems, viz. temperature and free energy. The entropy now appears as a derived quantity :

$$S = \log Z + \beta \bar{E} \qquad (21)$$

It is not surprising that this expression for the entropy is formally similar to that obtained in Ch. II, § 6 for the systems of identical elements with weak interactions : for, as already noted (see footnote at the end of § 2), the theory of such systems can be regarded as a special application of that of closed systems.+ However, the scope of formula (21) is much wider : it applies to any kind of system without restriction. If the system is sufficiently large to allow the use of the asymptotic expression for the measure of its energy surfaces, we may compare the value (21) of the entropy with the logarithm of the measure of the surface corresponding to the mean energy $\bar{E}$, viz.

$$\log \mu(\bar{E}) = \log\left\{\frac{Z(\beta)}{\sqrt{2\pi B}} e^{\beta \bar{E}}\right\} = S - \log\left(\sqrt{2\pi B}\right)$$

The logarithm of the fluctuation term is of a negligible order of magnitude, and we thus get a new interpretation of the entropy in terms of the

---

+ The system S then represents a single element, and the expression (21) accordingly gives the entropy per element.

measure of a set of phases : this set is not, however, the domain $\Omega(\bar{E})$ enclosed by the energy surface $\bar{E}$, but the surface itself. We have here another illustration of the "insensibility" of the entropy definition.

With the help of (21), we easily verify the well-known thermodynamic property, on which the phenomenological definition of the entropy rests, that the inverse temperature β is an integrating factor of infinitesimal quantity of heat supplied to the system in a quasi-static transformation. This quantity of heat is

$$Q = d\bar{E} - A da$$

whence

$$\begin{aligned} \beta Q &= d(\beta \bar{E}) - \bar{E}\, d\beta - \beta A da \\ &= d(\beta \bar{E}) + \frac{\partial}{\partial \beta} \log Z \, d\beta + \frac{\partial \log Z}{\partial a} da \end{aligned}$$

$$= d(\beta \bar{E}) + \log Z) = dS$$

Finally, let us introduce with Gibbs the concept of <u>probability exponent</u> which will give us not only a compact notation for canonical averages, but also exhibit a new aspect of our entropy definition. The canonical average of any phase function

$$\bar{f} = \frac{1}{Z} \int f(P)\, e^{-\beta H}\, d\mu$$

may be written as

$$\bar{f} = \int f(P)\, e^{\eta(P)}\, d\mu \qquad (22)$$

with

$$\eta(P;\, \theta, a) = \frac{1}{\theta}\left[F(\theta, a) - H(P;a)\right] \qquad (23)$$

The function η is called by Gibbs the "probability exponent", since

$$n(P;\, \theta,\, a) = e^{\eta} \qquad (24)$$

represents the density of probability in phase space for the canonical distribution. Now, the entropy, according to (16), is just minus the canonical average of the probability exponent :

$$S = -\bar{\eta} \;;$$

this may be written, with the notation (24)

$$S = -\int n \log n \; d\mu \qquad (25)$$

Again, we find here a formal analogy with Boltzmann's H-function for systems of weakly coupled elements. The expression (25) may be applied to quite general systems : it does not then refer however, to any actual distribution of physical elements, but to a purely fictitious distribution of "copies" of the system under investigation.

The statistical foundation of thermodynamics just outlined is not yet logically complete. The basic differential equation (17) refers essentially to quasi-static transformations. We have still to investigate the behaviour of the entropy when the system is subjected to irreversible transformations. But before this, we have a more immediate task. In the preceding discussion, all macroscopic quantities have been as a matter of course represented by canonical averages : this procedure, however, implies the assumption that the quasi-static transformations do not disturb the canonical form of the equilibrium distribution. Quasi-static transformations are of two distinct types : isothermal or adiabatic. For isothermal transformations, the assumption just mentioned is obviously justified, since the system remains in contact with the same thermostat during the transformation. But the case of adiabatic transformations requires a closer investigation. In fact, in such a transformation, the contact with the thermostat is initially severed, and at the end the temperature of the system has varied, i.e. it is in equilibrium with another thermostat : it is is then far from obvious that the distribution, while both external parameters and temperature varied, nevertheless rémained canonical. This is what we shall now proceed to show.

5.- Permanence of canonical distribution in quasi-static adiabatic transformations. An adiabatic transformation can be analysed as a succession of steps in which, the system being isolated, some external parameter (or set of parameters) a is varied suddenly by a very small amount da, after which the system is left to itself for a certain time. A second sudden variation of a is then applied and the process is repeated with suitably chosen intervals between the successive variations so as to approximate any continuous variation a(t) of the parameter a. In order for the transformation to be quasi-static, we must, after each small variation of a, allow sufficiant time to elapse for the system for the system to reach the state of equilibrium corresponding to the new value of the parameter : a quasi-static adiabatic transformation corresponds in this

sense to an infinitely show variation of a.

For our present purpose, it is of course sufficient to consider a single step, leading from a_o to $a = a_o + da$, and to show that if the initial distribution was canonical, with a certain temperature (or, in Gibbs' terminology, "modulus") θ_o, the final distribution is again canonical, with a slighty[1] different modulus. The variation of a has the effect of deforming the energy surfaces, so that a distribution which was originally ergodic ceases to have this property when referred to the new energy surfaces. Eventually, however, it will become ergodic on these new surfaces, and the new phase density will be given by the ergodic average of the old one, taken on the new energy surfaces: The initial phase density was given by $e^{\eta(\theta_o, a_o; pq)}$; the new one is accordingly $\overline{e^{\eta(\theta_o, a_o; pq)}}_{E(a)}$ We want to show that this quantity can again be written in the form of a canonical distribution of suitable modulus θ .

To this end, let us first expend the distribution density $e^{\eta(\theta_o, a_o; pq)}$ around the new value a of the parameter :

$$e^{\eta(\theta_o, a_o; pq)} = e^{\eta(\theta_o, a; pq)} \left[1 - \frac{da}{\theta_o}\left(A - \frac{\partial H}{\partial a}\right)\right]$$

and accordingly, since the factor $e^{\eta(\theta_o, a; pq)}$ is constant on the new energy surface E(a)

$$\overline{e^{\eta(\theta_o, a_o; pq)}}_{E(a)} = e^{\eta(\theta_o, a; pq)} \left[1 - \frac{da}{\theta_o}\left(A - \overline{A}_{E(a)}\right)\right]$$

Now, for systems with a large number of degrees of freedom, the canonical distribution has a sharp maximum for the average energy $\bar{E}$ and we may use the expansions

$$\overline{A}_E = \overline{A}_{\bar{E}} + \frac{\partial \overline{A}_{\bar{E}}}{\partial \bar{E}}(E - \bar{E}) + \frac{1}{2}\frac{\partial^2 \overline{A}_{\bar{E}}}{\partial \bar{E}^2}(E - \bar{E})^2$$

$$A = \overline{A}_{\bar{E}} + \frac{1}{2}\frac{\partial^2 \overline{A}_{\bar{E}}}{\partial \bar{E}^2}\overline{(E - \bar{E})^2}$$

The difference $A - \overline{A}_E$ will thus involve, besides a term linear in $E - \bar{E}$ a term containing

$$(E - \bar{E})^2 - \overline{(E - \bar{E})^2} = (E - \bar{E})^2 - B = \frac{\partial B}{\partial \bar{E}}(E - \bar{E})$$

owing to the small factor $\partial B / \partial \bar{E}$, this term will be negligible in comparison with the direct one, and we may therefore write

$$\overline{e^{\eta(\theta_o, a_o; pq)}}_{E(a)} \simeq e^{(\theta_o, a; pq)}\left[1 + \frac{\partial a}{\partial \theta_o}\frac{\partial \overline{A}_{\bar{E}}}{\partial \bar{E}}(E - \bar{E})\right]$$

It is now clear that the correction term in $E - \bar{E}$ can be compensated by a suitable change of modulus; for if we pass from θ_o to $\theta = \theta_o + d\theta$,

we have, using Helmholtz's formula,

$$e^{\eta(\theta_0, a; pq)} = e^{\eta(\theta, a; pq)} \left[1 - \frac{d\theta}{\theta^2}(E - \bar{E})\right]$$

We conclude that the final distribution is indeed the canonical one of modulus θ, provided that the variation $d\theta$ of modulus is related to the variation da by the equation

$$\frac{\partial \theta}{\theta_0} - \frac{\partial \bar{A}|\bar{E}}{\partial \bar{E}} da = 0$$

Replacing $\bar{A}|_{\bar{E}}$ by A and θ_0 by θ, and noting, at constant a,

$$\frac{\partial A}{\partial \bar{E}} = \frac{\partial A}{\partial \theta} \Big/ \frac{\partial \bar{E}}{\partial \theta},$$

the last equation may be written

$$\frac{1}{\theta} \frac{\partial \bar{E}}{\partial \theta} d\theta - \frac{\partial A}{\partial a} da = 0$$

It is readily verified * that this equation just expresses the constancy of the entropy, $dS = 0$, during the transformation.

6.- Irreversible transformations. The last step in establishing the statistical foundation of thermodynamics consists in verifying that our interpretation of the entropy as minus the average probability exponent of the canonical distribution satisfies the part of the second law referring to irreversible transformations. We must show that for any transformation such that the surrendings of our system to their initial state after it is performed, the entropy of the final state of the system is larger (or at any rate not smaller) than that of the initial state; if we formulate the law in terms of average probability exponents, the direction of the inequality is reversed. It must be observed that a probability exponent which would correspond to an equilibrium state under certain conditions represents an arbitrary density distribution if these conditions are altered. We shall thus have to introduce, following Gibbs, arbitrary probability exponents $\varpi(P)$ and study the behaviour of their average values.

$$\bar{\varpi} = \int \varpi e^{\varpi} d\mu$$

under the various transformations satisfying the above-mentionned condition.

---

* In fact, from (18) it follows that

$$-\frac{\partial A}{\partial \theta} = \frac{\partial S}{\partial a}$$

and from (19) that

$$\frac{1}{\theta} \frac{\partial E}{\partial \theta} = -\frac{\partial^2 F}{\partial \theta^2} = \frac{\partial S}{\partial \theta}$$

All such transformations reduce t two types : (a) the adiabatic transformations, during which the system is thermally isolated, (b) the heat exchange, in which two initially separated systems are brought into thermal contact and separated again. We shall discuss these two types in succession, closely following Gibbs' elegant treatment of the problem.

(a) Adiabatic transformations. During an adiabatic transformation, the distribution changes independently in each energy shell : we shall thus compare distributions with the same total number of "copies" of the system in the same energy shell, and prove that the distributions with probability exponent ϖ_0 constant in each energy shell have a smaller average probability exponent than the others. We call this statement the first lemma of Gibbs. The assumption is

$$\int_{[E]} e^{\varpi} d\mu = \int_{[E]} e^{\varpi_0} d\mu$$

for each energy shell $[E]$. For the average of ϖ_0 over a shell we may thus write

$$\int_{[E]} \varpi_0 e^{\varpi_0} d\mu = \varpi_0 \int_{[E]} e^{\varpi_0} d\mu = \varpi_0 \int_{[E]} e^{\varpi} d\mu = \int_{[E]} \varpi_0 e^{\varpi} d\mu ,$$

and therefore $\bar{\varpi}_0 = \int \varpi_0 e^{\varpi} d\mu$

We must now prove that

$$\bar{\varpi} - \bar{\varpi}_0 = \int (\varpi - \varpi_0) e^{\varpi} d\mu \geqslant 0$$

Gibbs uses here a general procedure applicable to any inequality of the form $-\int \varkappa e^{\varpi} d\mu \geqslant 0$. He refers this inequality to a property of the exponential function :

$$e^x - 1 - x \geqslant 0 \text{ for any } x.$$

To this end, he uses the normalization conditions to show that the appropriate terms $e^{x} - 1$ associated to $-x$ have the average 0. In the present instance $-x = \varpi - \varpi_0$; from the normalization conditions

$$\int e^{\varpi} d\mu = \int e^{\varpi_0} d\mu = 1$$

it indeed follows that

$$\int e^{\varpi} \left[e^{\varpi_0 - \varpi} - 1 \right] d\mu = 0$$

Adding this to the expression $\int (\varpi - \varpi_0) e^{\varpi} d\mu$, we immediately conclude that this quantity is always $\geqslant 0$.

Gibbs's lemma can now be applied successively to each step da of the adiabatic variation of the parameter a from a_q to a_n (§5).

Calling $\varpi_1, \varpi_2, \ldots, \varpi_n$ the successive probability exponents, we have

$$\overline{\varpi}_1 \geq \overline{\varpi}_2 \geq \cdots \geq \overline{\varpi}_n$$

If the transformation is quasi-static, the differences $\overline{\varpi}_1 - \overline{\varpi}_2$ are of the second order in da, and since the number of steps is inversely proportional to da, the difference $\overline{\varpi}_1 - \overline{\varpi}_n$ after a finite variation of a is infinitesimal : the entropy in this case remains constant. If, on the other hand, the transformation is irreversible, the successive differences will in general be of order da, and for a finite variation of a there will be a finite increase of the entropy.

(b) Heat exchange. To discuss the case of heat exchange we have to consider a system composed of two distinct parts S_1, S_2; we accordingly distinguish the two phase spaces of these parts and the total phase space which is their direct product. Between the respective elements of measure we have the relation

$$d\mu_1 \cdot d\mu_2 = d\mu$$

The distribution e^{ϖ} defines the distributions in the S_1, and S_2 spaces as

$$e^{\varpi_1} = \int e^{\varpi} d\mu_2 \qquad e^{\varpi_2} = \int e^{\varpi} d\mu_1 \; ;$$

these partial distributions are, of course, normalized to unity :

$$\int e^{\varpi_1} d\mu_1 = \int e^{\varpi_2} d\mu_2 = \int e^{\varpi} d\mu = 1$$

Gibbs' second lemma states that

$$\overline{\varpi} \geq \overline{\varpi}_1 + \overline{\varpi}_2$$

the inequality holding only if the two distributions ϖ_1, ϖ_2 are entirely independent, so that $\varpi = \varpi_1(P_1) + \varpi_2(P_2)$

To prove the lemma, note that

$$\overline{\varpi}_1 = \int \varpi_1 e^{\varpi_1} d\mu_1 = \int \varpi_1 e^{\varpi} d\mu \quad , \quad \overline{\varpi}_2 = \int \varpi_2 e^{\varpi} d\mu$$

and therefore

$$\overline{\varpi} - \overline{\varpi}_1 - \overline{\varpi}_2 = \int (\varpi - \varpi_1 - \varpi_2) e^{\varpi} d\mu$$

The normalization conditions give

$$\int e^{\varpi} \left[e^{\varpi_1 + \varpi_2 - \varpi} - 1 \right] d\mu = 0$$

whence the announced inequality follows. Moreover, the equality is seen to hold only if $\varpi - \varpi_1 - \varpi_2 = 0$, as stated.

With the help of this lemma, the discussion of the thermal contact of two systems is immediate. Before the contact, we have independent distributions with exponents ϖ_1, ϖ_2 and the exponent of the total distri-

bution is $\varpi = \varpi_1 + \varpi_2$. As a result of the thermal contact (during which the total system is isolated) the exponent changes from ϖ to ϖ' and by the first lemma

$$\bar{\varpi} \geq \bar{\varpi}'$$

Now, we had on the one hand

$$\bar{\varpi} = \bar{\varpi}_1 + \bar{\varpi}_2,$$

and on the other, by the second lemma

$$\bar{\varpi}' \leq \bar{\varpi}_1' + \bar{\varpi}_2',$$

ϖ_1', ϖ_2' being the exponents of probability of the two systems in their final states. Therefore

$$\varpi_1 + \varpi_2 \geq \varpi_1' + \varpi_2' \qquad (26)$$

i.e. the heat exchange has caused the sum of the entropies of the two systems to increase.

It is interesting to analyse somewhat more closely the role of the temperature in the phenomena of heat exchange. The basis for such an analysis is supplied by a third lemma of Gibbs : If θ is a positive parameter, the quantity $\bar{\varpi} + (\bar{E} / \theta)$ is minimum for the canonical distribution of modulus θ. For the latter distribution, the quantity in question is just F / θ ; the lemma thus expresses a mimimum property of the free energy of a system of given temperature, which is parallel to the maximum property of the entropy of an isolated systen. We have to prove

$$\int \left(\varpi + \frac{E}{\theta} \right) e^{\varpi} d\mu - \frac{F}{\theta} \geq 0 \quad , \quad \text{i.e.} \quad \int (\varpi - \eta) e^{\varpi} d\mu \geq 0 \quad ,$$

η being the probability exponent of the canonical distribution of modulus θ. By the usual procedure, we derive from the normalization conditions

$$\int e^{\varpi} \left[e^{\eta - \varpi} - 1 \right] d\mu = 0$$

whence the preceding inequality follows.

Suppose one of the two systems just considered is a "thermostat" of temperature θ_2 . Besides the inequality (26) we may now write, by the third lemma

$$\bar{\varpi}_2 + \frac{\bar{E}_2}{\theta_2} \leq \bar{\varpi}_2 + \frac{\bar{E}_2}{\theta_2}$$

since the initial state was described by a canonical distribution of modulus θ_2 . Therefore

$$\varpi_1 - \varpi_2' \geq \frac{\bar{E}_2 - \bar{E}_2'}{\theta_2} \quad , \qquad (27)$$

or in terms of thermal quantities

$$S_1' - S_1 \geq \frac{Q}{\theta_2} \quad ,$$

i.e. the entropy increase of a system brought in contact with a thermostat of temperature θ_2 is at least Q/θ_2, where Q is the quantity of heat passing tfrom the thermostat to the system. Using

$$\bar{E}_2 - \bar{E}_2' = \bar{E}_1' - \bar{E}_1$$

we can also write the inequality (27) in the form

$$\bar{\varpi}_1 + \frac{\bar{E}_1}{\theta_2} \geqslant \bar{\varpi}_1' + \frac{\bar{E}_1'}{\theta_2}$$

showing how the quantity $\bar{\varpi} + (\bar{E}/\theta_2)$ pertaining to the system S_1 deareases after thermal contact with the thermostat, until, by repoated or prolonged contact, the canonical distribution of modulus θ_2 is reached, and with it the minimum value of the quantity in question, which is then the free energy of the system.

We may finally consider a system S_0 undergoing a cycle of transformations in which it comes successively in contact with various thermostats of temperature θ_1, θ_2.... Assuming S_0 to be initially at temperature θ_0, we have

$$\bar{\varpi}_0 + \bar{\varpi}_1 + \bar{\varpi}_2 + \ldots \geqslant \bar{\varpi}_0' + \bar{\varpi}_1' + \bar{\varpi}_2' + \ldots$$

$$\bar{\varpi}_i' + \frac{\bar{E}_i'}{\theta_i} \geqslant \bar{\varpi}_i + \frac{\bar{E}_i}{\theta_i} \qquad (i = 0, 1, 2, \ldots)$$

whence

$$\frac{\bar{E}_1 - \bar{E}_1'}{\theta_1} + \frac{\bar{E}_2 - \bar{E}_2}{\theta_2} + \ldots \leq 0 \qquad (28)$$

the term pertaining to the system S_0 has disappeared since $\bar{E}_0' = \bar{E}_0$ owing to the cyclic character of the transformation. The inequality (28) coincides with an important theorem proved by Clansius and used by him for establishing on a phenomenological basis the concept of entropy. If there are only two thermostats, we have the kind of idealized engines considered by Carnot. Calling Q_1, Q_2 the algebraic quantities of heat supplied by the thermostats during a cycle, inequality (28) takes the form

$$\frac{Q_1}{\theta_1} + \frac{Q_2}{\theta_2} \leq 0$$

If the heat transfers are irreversible and not accompanied by any mechanical work, e.g. if heat is conducted or radiated through the system S_0, we have $Q_1 = -Q_2$ and the inequality merely expresses the fact that heat passes irreversibly from the hot to the cold thermostat. If an amount of mechanical work $W = Q_1 + Q_2$ is supplied by the engine ($\theta_1 > \theta_2$; $Q_1 > 0$), we find for the efficiency the wellknown expression $\frac{W}{Q_1} < \frac{\theta_1 - \theta_2}{\theta_1}$, the equality corresponding to Carnot's reversible engine.

IV.- STATISTICS OF OPEN SYSTEMS.

1. Phase functions and averages for open systems. Our last object of investigation is the statistical description of systems consisting of a variable number of elements. Since the main application of this theory is the study of chemical reactions, we shall speak of systems of "molecules". We start from the μ -spaces of the single molecules, from which we construct by direct product the Γ -spaces corresponding to any given numbers of molecules of the various species occuring in the system considered. In the following, we shall only treat the case of a mixture of two distinct constituents, which is sufficiently typical. We denote by $P_{N_1N_2}$ the set of coordinates of the Γ -space corresponding to N_1 molecules of the first species and N_2 molecules of the other.

The definition of phase functions requires some care. In general, a physical quantity pertaining to a system of N molecules of the same species may be expressed in terms of other quantities attached either to a single molecule or to a pair of molecules or, more generally, to a cluster of any number of molecules. It can thus be written in the form

$$f(P_N) = \sum_{i=1}^{N} f^{(1)}(P_i) + \sum_{i=1}^{N} \sum_{k=1}^{N} f^{(2)}(P_i, P_k) + \ldots \qquad (1)$$

where P_i denotes a phase in the μ -space of the i-th molecule. The extension of this definition to the case of a mixture of molecules is immediate ; it gives a well-defined meaning to the notation $f(P_{N_1N_2})$.

In order to compute the statistical average of such a phase function for an open system, we follow the same line of argument as for closed systems ; we consider our system in conjuction with the requisite number of very large reservoirs of molecules of the different species, so that the total system may be regarded as closed. For the closed system, which we assume to have a definite temperature, we may write down the canonical average of the phase function. there then remains the task of elimina - ting the variables pertaining to the reservoirs. The exchange of molecules between the system S containing a mixture of different species and any reservoir R containing one definite species must be imagined to take place through a suitable semi-permeable membrane : the physical existence of such membranes, however, is not relevant to the argument; it suffices that the concept of semi-permeable membrane be logisally consistent with the basic

assumptions of the atomic theory of matter.

The phase functions referred to the closed system $S + R_1 + R_2$ are themselves statistical averages over all passible distributions of the molecules between the system S and the appropriate reservoir. With respect to each species of molecules, the system S can be regarded as a small part of the corresponding large reservoir ; the law of distribution of molecules in S therefore takes the asymptotic form of a Poisson distribution.*

$$w(N) = \frac{\bar{N}^N}{N!} e^{-\bar{N}} \qquad (2)$$

$\bar{N}$ being the average number present in the system S. Thus, the phase function whose canonical average is needed is

$$\sum_{N_1, N_2} w(N_1)\, w(N_2)\, f(P_{N_1 N_2}), \qquad (3)$$

with the definition (1) of $f(P_{N1N2})$. Here, $f(P_{N1N2})$ de pends only on the variables of the system S. We have also to consider the total Hamiltonian of the closed system $S + R_1 + R_2$, which we may take to be the sum of the Hamiltonians of the three parts : $H + H_{R1} + H_{R2}$. For any distribution of the molecules, characterized by the numbers N_1, N_2, we have, more explicitly,

$$H(P_{N1N2}) + H_{R1}(P_{N1}') + H_{R2}(P_{N2}') \qquad (4)$$

where P_{Ni}' denotes the phase of the reservoir R_i containing N_i' molecules. If N_i represents the total number of molecules of species i, we have $N_i' = \mathcal{N}_i - N_i$, so that the phase function of the more general type (4) is also specified by the numbers N_1, N_2 of molecules in the system S.

The statistical weight of the phase P_{N1N2} of the system S is therefore proportional to

$$d\mu_{N_1 N_2}\, e^{-\beta H(P_{N_1 N_2})} \int e^{-\beta [H_{R_1}(P_{N_1'}) + H_{R_2}(P_{N_2'})]}\, d\mu_{N_1'}\, d\mu_{N_2'},$$

i.e.

$$d\mu_{N_1 N_2}\, e^{-\beta H(P_{N_1 N_2})}\, Z_{R_1}(\mathcal{N}_1 - N_1)\, Z_{R_2}(\mathcal{N}_2 - N_2),$$

where $Z_{R_i}(N_i')$ represents the "sum over states" for the reservoir R_i containing N_i' molecules. Denoting the corresponding sum over states for the system by $Z(N_1, N_2)$, we finally get for the canonical average of any phase function pertaining to the system S the expression

---

* We might even take a Gaussian distribution, but the choice of the Poisson distribution is somewhat more general and fits in better with the thermodynamical formulae.

$$\bar{f} = \frac{\sum_{N_1,N_2} W(N_1)W(N_2) Z_{R_1}(\mathcal{N}_1-N_1) Z_{R_2}(\mathcal{N}_2-N_2) \int f(P_{N_1,N_2})\, e^{-\beta H(P_{N_1,N_2})}\, d\mu_{N_1,N_2}}{\sum_{N_1,N_2} W(N_1)W(N_2) Z_{R_1}(\mathcal{N}_1-N_1) Z_{R_2}(\mathcal{N}_2-N_2) Z(N_1,N_2)}$$

In this formula, the parameters defining the external conditions under which the system is considered are, besides the temperature and the non-thermal parameters of type a, the <u>average</u> numbers $\bar{N}_1$, $\bar{N}_2$ of molecules in the system (which, however, are not necessarily all independent).

2.- <u>Chemical potentials</u>. The problem now confronting us is to find some simple asymptotic expression for the dependence of the function $Z_{R_i}(N_i')$, representing the reservoirs in formula (5), on the numbers N_i' of molecules contained in them. Since the total numbers $\mathcal{N}_i$ can be made arbitrarily large, we are actually interested only in small <u>relative</u> deviations $(N_i' - \bar{N}_i') / \bar{N}_i'$ of the numbers N_i' from their average values $\bar{N}_i' = \mathcal{N}_i - \bar{N}_i$. Even the absolute fluctuations $N_i' - \bar{N}'_i = -(N_i - \bar{N}_i)$ may be restricted in magnitude; for the contributions of terms corresponding to large fluctuations are in any case cut down by the distribution factors $W(N_i)$. The situation here is entirely similar to that we had when discussing the energy fluctuations in the interaction of a closed system with a thermostat. We have thus to compare each $Z_{R_i}(N_i')$ with its average value $Z_{R_i}(\bar{N}_i')$ for relatively small differences $N'_i - \bar{N}_i'$, and in order first to obtain the dependence of the latter function on the average number $\bar{N}_i'$ we shall make use of the fact that $\log. Z_{R_i}(N_i')$ is directly connected with the free energy of the system R_i. The following argument is essentially due to Tolman *.

To present the matter as simply as possible, we shall first consider in general terms the question of how the macroscopic variables describing a system of identical elements depend on the number of these elements. From this point of view the variables fall into two classes. Some of them, called <u>intensive</u> variables, are independent of the number of elements they characterize properties which belong to any part of the system and are uniform throughout; such are, for instance, the pressure and the temperature. Other variables, the <u>extensive</u> ones, are proportional to the number of elements; they describe those properties of the homogeneous system which are due to additive contributions from the various par of it; examples of extensive variables are the volume, the mean energy, and the characteristic functions : entropy and free energy. Extensive variables give rise to

* Cf R. Tolman, Phys. Rev. 57, 1160, 1940

corresponding "densities", which are again intensive variables : the density is the partial derivative of the extensive variable with respect to the number of elements, provided that the other independent variables, kept constant in the derivation, are all intensive.

It is always possible to have all independent variables intensive, for each pair a, A consists of an extensive and an intensive variable, either of which can be chosen as representative of the corresponding physical phenomenon. Thus, we may take either the volume or the pressure as the mechanical variable of a body of isotropics structure; there are accordingly two different "free energies" $F(\theta, V)$ and $G(\theta, p)$ which are usually associated, in a rather arbitrary fashion, with the names of Helmholtz and Gibbs, respectively. In general, the passage from the characteristic function $F(\theta, a)$ to the function $G(\theta, A)$ is affected by a "Legendre transformation" :

$$G(\theta, A) = F[\theta, a(A)] - a(A).A,$$

where $a(A)$ is the inversion of the function $A(a)$ computed from $F(\theta, a)$ Thus, $G(N; \theta, p) = F(N; \theta, V) + Vp$, and the corresponding density is

$$g(\theta, p) = \left(\frac{\partial G}{\partial N}\right)_{\theta, p} \qquad (6)$$

so that

$$G(N; \theta, p) = N\, g(\theta, p) \qquad (7)$$

From the connexion

$$\log Z(N; \theta, p) = -\beta G(N; \theta, p)$$

between the statistical function $\log Z$ and the characteristic function G we derive immediately

$$\log Z(N; \theta, p) = -N\beta g(\theta, p)$$

i.e. $\log Z$ is an extensive function. This formula, it is true, is not strictly applicable to the case of our reservoirs, because the variation of the number of molecules in such a reservoir does not occur in an externally controlled way, at constant pressure, but as the result of random fluctuations. The pressurein the reservoir is regulated by the mechanical equilibrium conditions across the semi-permeable membrane through which the exchange of molecules with the system S takes place; its value is thus a function of the average numbers $\overline{N}_1$, $\overline{N}_2$ of molecules in the system S, and every deviation from these averages brings about a perturbation of the equilibrium. For <u>small</u> deviations, however, we may write :

$$\log \frac{Z_{R_i}(N_i', \theta, p)}{Z_{R_i}(\bar{N}_i', \theta, p)} = -(N_i - \bar{N}_i')\beta g_i(\theta, p)$$

$$= (\bar{N}_i - N_i)\beta g_i(\theta, p),$$

where the reservoir pressure p_i is a function of the pr[illegible] p of the system S and of the average numbers $\bar{N}_1$, $\bar{N}_2$. Apart from a factor independent of N_i, and which therefore cancels out in the average (5) of the phase function f, we have the required asymptotic expression

$$Z_{R_i}(N_i - N_i) \sim e^{-\beta g_i N_i}$$

Combining this with the factor μ^{N_i} (N_i), given by (2); we may say that in the average (5), each number N_i is weighted by a factor of the form

$$\frac{1}{N_i!} e^{\beta \xi_i N_i}$$

where the function $\xi_i(\theta, p; \bar{N}_1, \bar{N}_2) = -g_i + \theta \log \bar{N}_i$ represents the reservoir R_i in the same way as the parameter θ represents the thermostat. In view of its fundamental importance for the determination of chemical equilibria, it is usually called the chemical potential of the molecular species i in the system S.

The average (5) of the phase function f now takes the form

$$\bar{f} = \frac{\sum_{N_1 N_2} \frac{1}{N_1! N_2!} e^{\beta(\xi_1 N_1 + \xi_2 N_2)} f(p_{N_1 N_2}) e^{-\beta H(p_{N_1 N_2})} d\mu_{N_1 N_2}}{\sum_{N_1 N_2} \frac{1}{N_1! N_2!} e^{\beta(\xi_1 N_1 + \xi_2 N_2)} Z(N_1, N_2)} \quad (8)$$

The phase integrations indicated by $d\mu_{N_1 N_2}$ are over specif[illegible] phases, and the factor $(N_1!\, N_2!)^{-1}$ has the effect of reducing them to integrations over generic phases, in which each physical configuration of the system is counted only once. The introduction of this reduction factor was presented by Gibbs as a matter of convention, justified by its success, and it has since given rise to much confuse discussion : the present derivation** shows how naturally it comes in when a physical point of view is adopted, in contrast to the more abstract attitude of Gibbs.

** On this point even Tolman's paper, which we followed in all other particulars, is not sufficiently explicit.

* It is easily found (see : Tolman's paper) that the effect of the perturbation of the equilibrium is of the order $(N_i' - \bar{N}_i) / \bar{N}_i'$

According to formula (8), the average f can be described as a canonical average over generic phases for each possible set of numbers of molecules, weighted by an exponential distribution factor exp $[\beta(\xi_1 N_1 + \xi_2 N_2)$ there is a complete analogy with the concept of canonical average itself which is an ergodic average over each energy surface, weighted by an exponential factor exp $[-\beta H]$. Hence the somewhat awkward nomenclature proposed by Gibbs : the ordinary canonical distribution of copies of a closed system forms a "petit ensemble"; the distribution just found for an open system is a "grand ensemble". It is often, more simply called a grand canonical distribution.

3.- Thermodynamics of open systems. The statistical interpretation of the thermodynamical functions for open systems is a straight forward extension of the theory of closed systems, but it adds an aspect of fundamental importance in chemistry, viz. the way in which the characteristic functions depend on the numbers of molecules of various species present in the system; We are here concerned, of course, with the equilibrium states of the system, and therefore with the average numbers of molecules. Let us assume, for definiteness, that the independent mechanical variable is the pressure; the characteristic function will thus be the Gibbs free energy.

Let us put

$$\mathcal{Z}(\bar{N}_1, \bar{N}_2) = \frac{1}{N_1! N_2!} Z(N_1, N_2) \qquad (9)$$

For a system with fixed numbers of molecules N_1, N_2, we may define the free energy by

$$G(N_1, N_2) = -\theta \log \mathcal{Z}(N_1, N_2) : \qquad (10)$$

this differs from our previous definition only by a constant term without interest so long as the numbers of molecules do not vary. Let us now consider the denominator of our fundamental formula (8) :

$$e^{-\Omega} = \sum_{N_1, N_2} \mathcal{Z}(N_1, N_2)\, e^{\beta(\xi_1 N_1 + \xi_2 N_2)} , \qquad (11)$$

and differentiate it N_1, N_2 with respect to all macroscopic variables: this differentiation includes the average numbers $\bar{N}_1$, $\bar{N}_2$, but leaves out the numbers N_1, N_2, over which a summation is performed. We get

$$-d\Omega = e^{\Omega} \sum_{N_1,N_2} Z(N_1,N_2)\, e^{\beta(\xi_1 N_1 + \xi_2 N_2)} \left[d \log Z(N_1,N_2) + N_1 d(\beta\xi_1) + N_2 d(\beta\xi_2) \right]$$

$$= -d\left[\overline{\beta G(N_1,N_2)}\right] + \bar{N}_1 d(\beta\xi_1) + \bar{N}_2 d(\beta\xi_2),$$

where the averages refer to the distribution of the numbers N_1, N_2 given by the probability law

$$e^{\Omega} Z(N_1 N_2)\, e^{\beta(\xi_1 N_1 + \xi_2 N_2)}$$

The last equation may also be written

$$d\left[\Omega + \beta\xi_1 \bar{N}_1 + \beta\xi_2 \bar{N}_2\right] = d\left[\overline{\beta G(N_1,N_2)}\right] + \beta\xi_1 d\bar{N}_1 + \beta\xi_2 d\bar{N}_2 \qquad (12)$$

which shows that the characteristic function in terms of the independent variables θ, $\beta\xi_1$, $\beta\xi_2$ is $\Omega + \beta(\xi_1 \bar{N}_1 + \xi_2 \bar{N}_2)$.

If, in the right hand side of equation (11) we replace the sum over the N_i's by the single term corresponding to the values $\bar{N}_1$, $\bar{N}_2$ of these numbers, we derive from it an approximate form of the characteristic function,

$$\Omega + \beta(\xi_1 \bar{N}_1 + \xi_2 \bar{N}_2) \approx \beta G(\bar{N}_1, \bar{N}_2) \qquad (1.)$$

according to (10). To this approximation, which is justified provided that the numbers $\bar{N}_1$, $\bar{N}_2$ are very large, we thus see that the characteristic function is still the freeeenergy [*], taken for the average numbers of molecules, even when these average numbers are varied independently. Now; however, we see that it is quite essential to introduce the factor $(N_1!\, N_2!)^{-1}$, whose role is to reduce the "sum over states" to the physically distinct states of the system, represented by generic phases. Indeed, it is only when the integration is reduced to generic phases that the free energy of a system of identical elements preserves its extensice character when a subdivision of the system into parts is taken into consideration. For if we make such a subdivision into two parts containing N_A and N_B elements, respectively, and consider the sums over state $Z(N_A + N_B)$, $Z(N_A)$ $Z(N_B)$, integrated over all specific phases of the total system and of the two parts separately, we have

$$Z(N_A + N_B) = \frac{(N_A + N_B)!}{N_A!\, N_B!}\, Z(N_A)\, Z(N_B)$$

---

[*] The factor β can evidently be retained or omittes without changing the property of the function of being a "characteristic" one.

i.e. precisely

$$\mathcal{Z}\,(N_A + N_B) = \mathcal{Z}(N_A)\,\mathcal{Z}(N_B).$$

The argument is immediately extended to the more general case we are considering of homogeneous systems containing several species of molecules. We must only generalise the concept of extensive and intensive functions : these will denote homogeneous functions of the numbers of molecules, of degree 1 and 0, respectively.

Using the approximation (13) we get from (12) the fundamental relation

$$\zeta_i = \left(\frac{\partial G}{\partial \bar{N}_i}\right)_{T,p,\{\bar{N}_i\}} \qquad (14)$$

the symbol $\{\bar{N}_i\}$ indicating that all $\bar{N}_k$'s except $\bar{N}_i$ are kept constant in the derivation. The extensive character of G allows us to write

$$G = \sum_i \bar{N}_i \frac{\partial G}{\partial \bar{N}_i} = \sum_i \bar{N}_i \zeta_i \qquad (15)$$

Comparing (15) with (13), we see that, to the approximation considered, $\Omega \approx 0$. This means that the denominator of formula (8) pratically reduces to unity, which considerably simplifies this formula.

An interesting feature of the free energy for a mixture of molecules is that it does not reduce to the expression for a single species if the different kinds of molecules are identified. Take e.g. the simple case of a mixture of two species of molecules in the ideal gas state. We have

If we identify the molecules $Z_1 = Z_2 = Z$, the two first terms reduce to the expected form $-(N_1 + N_2) \log Z$, but the last one is different from $-\log (N_1 + N_2)!$. This "Gibbs paradox" shows how essential it is for a consistent treatment of systems of various kinds of elements that theses elements be distinguished by <u>discontinuous</u> criteria. Of course, the selection of those marks which will be used to distinguish different species is a matter of convention, to be decided according to the circumstances of the concrete problem at hand. Thus, in ordinary chemical reactions, isotopes must be treated as identical elements, whereas in questions of isotope separation they will naturally be distinguished into different species by taking into consideration the mass differences which are neglected <u>in principle</u> for the definition of chemical species.

4.- Characteristic functions involving the temperature. In the preceding section, we have chosen as independent variables, besides the temperature, the pressure and the numbers of molecules : we have seen that the corresponding characteristic function is the free energy $G(\theta, p, \bar{N})$ in the sense of Gibbs. Always keeping the temperature as the independent thermal parameter, we have in principle 3 other possible combinations for the mechanical and chemical variables, according as we choose the volume instead of the pressure and the chemical potentials instead of the numbers of molecules. It is easy to construct the characteristic functions for all these cases, by applying the suitable Legendre transformations. To begin with, we can eliminate the choice of θ, p, ζ as independent variables, for the characteristic function would then become $G - \sum_i \bar{N}_i \zeta_i$, i.e. by (15), identically zero. There accordingly remain 3 possibilities, viz.*

$$\begin{aligned} G(\theta, p, \bar{N}) &= \sum_i \bar{N}_i \zeta_i \\ F(\theta, V, \bar{N}) &= \sum_i N_i \zeta_i - pV \\ \Omega(\theta, V, \zeta) &= -pV \end{aligned} \tag{16}$$

The property of being a characteristic function is expressed in the three cases by similar equations :

$$\begin{aligned} dG &= -S d\theta + V dp + \sum_i \zeta_i d\bar{N}_i \\ dF &= -S d\theta - p dV + \sum_i \zeta_i d\bar{N}_i \\ d\Omega &= -S d\theta - p dV - \sum_i \bar{N}_i d\zeta_i \end{aligned} \tag{17}$$

Thus, we see that the chemical potentials can be defined by

$$\zeta_i = \left(\frac{\partial F}{\partial \bar{N}_i}\right)_{\theta, V; \{\bar{N}_i\}} \tag{18}$$

just as well as by (14). On the other hand, we have

$$\bar{N}_i = -\left(\frac{\partial \Omega}{\partial \zeta_i}\right)_{\theta, V; \{\zeta_i\}} \tag{19}$$

The statistical definitions of the characteristic functions Ω, F, G, are likewise quite parallel : the present co mon feature of

* The function Ω in (16) has a diffe ent meaning from the function denoted by the dame letter in section 3. Henceforth, Ω will always denote the function defined in (16).

being simply related to the normalisation factors of the respective statistical distributions. The definition of Ω is in fact given by

$$e^{-\beta\Omega} = \sum_{N_1 N_2 \cdots} \frac{e^{\beta \sum_i \gamma_i N_i}}{N_1!\, N_2! \cdots} \int e^{-\beta H(P_{N_1 N_2 \cdots}; V)}\, d\mu_{N_1 N_2 \cdots} \tag{20}$$

where the Hamiltonian is expressed in terms of the volume as the external mechanical variable; the proof is immediately obtained* by computing the differential of Ω with respect to the independent variables θ, V and the γ_i's. From (20) and (16) we derive for the function F the equation

$$e^{-\beta F} = \sum_{N_1 N_2 \cdots} \frac{e^{\beta \sum_i \gamma_i (N_i - \bar{N}_i)}}{N_1!\, N_2! \cdots} \int e^{-\beta H(P_{N_1 N_2 \cdots}; V)}\, d\mu_{N_1 N_2 \cdots} \tag{21}$$

if we neglect the fluctuations of the numbers N_i around their averages $\bar{N}_i$ this expression reduces to

$$e^{-\beta F} \approx \frac{1}{\bar{N}_1!\, \bar{N}_2!} \int e^{-\beta H(P_{\bar{N}_1 \bar{N}_2 \cdots}; V)}\, d\mu_{\bar{N}_1 \bar{N}_2 \cdots} \tag{22}$$

Now, the corresponding rigorous and approximate expressions for the function G are the same as those for F, except that the Hamiltonian must now be expressed in terms of p. This corresponds, for the macroscopic quantities, to the passage from the "energy" to the "enthalpy" of the system. From the atomistic point of view, we have

$$H(P; p) = H(P; V) + p\bar{V} \tag{23}$$

the physical meaning of this relation is that in this passage we change the definition of the mechanical system considered. In fact, if the volume is given, the Hamiltonian is simply the energy of the system of molecules enclosed in a fixed container. If the pressure is given, we must imagine that, for instance, one wall of the container is a movable piston, upon which the external pressure is exerted: this piston is now part of the system and contributes a term pV to the Hamiltonian (where V is now regarded as a function of p and the other independent macroscopic variables.)

---

* The situation is very similar to the above discussion of equation (11); but there, we had chosen the pressure as independent variable, which eventually led to the result that the other characteristic function Ω defined by (11) vanishes.

Seconde Partie

Chapter I.- QUANTAL DESCRIPTION OF PHYSICAL SYSTEMS.

1.- The states of a physical system. We shall here briefly recall the main features of the quantal mode of description of physical systems in the form best adapted to the application of statistical considerations; we shall especially have in view the definition of an invariant measure in the "space" in which the states of such systems are represented.

As is well-known, the most general way of characterizing the state of a system is by a complex vector in a Hilbert-space, i.e. a linear space in which the operation of scalar product of two vectors is defined. This operation plays a fundamental part in the physical interpretation : it makes possible the normalization of state vectors, by equating the scalar product of the vector by itself to unity; for two such normalized vectors, the square of the modulus of the scalar product gives the probability of ascertaining one of the states when the system is in the other.

Finally, one can specify the Hilbert space somewhat further by assuming that it contains complete orthogonal systems of state vectors; such systems form enumerable sequences of vectors. Every state vector can be expressed as a superposition of all the vectors of any complete orthogonal system. Let (f,g) denote the scalar product of any two vectors f;g; it is defined in such a way that $(g,f) = (f,g)^*$, the complex conjugate of (f,g). An orthogonal system φ_i of normalized state vectors is defined by the equations $(\varphi_i, \varphi_k) = \delta_{ik}$. If it is complete, we may write any state vector f in the form

$$f = \sum_i (f, \varphi_i)\, \varphi_i . \qquad (1)$$

---

* For such a treatment, see von Neumann's treatise.

2.- Physical quantities and operators in Hilbert space.

Physical quantities are represented by linear operators in Hilbert space : the quantity A acts upon the state vector f to transform it into another state vector Af, whose physical interpretation is fixed by saying that the scalar product (Af,f) represents the expectation value of the quantity A in the state f. In order that this expectation value be real, the operator A must satisfy the condition (Af, f) = (f, Af) for any f; such operators are called Hermitian. Physical quantities always correspond to Hermitian operators.

Besides the expectation value of a physical quantity in a given state, one can define the distribution of the possible values of this quantity in the state in question. This is the problem of main interest to us, since the distribution will give us the specification of measure we need for the study of statistical averages of the most general kind. We shall therefore go into some detail about it, without, however, aiming at a complete treatment.* We start with a class of Hermitian operators such that it is possible to find states in which they have a definite value : the eigenstates and corresponding eigenvalues of the operators. An eigenstate φ_i of the operator A, with eigenvalue a_i, is defined by

$$A\varphi_i = a_i \varphi_i \qquad (2)$$

From equation (2) it follows that any two eigenstates corresponding to distinct eigenvalues are orthogonal. Further, if an eigenvalue is degenerate, i.e. corresponds to a finite set of eigenstates, such a set can always be "orthogonalized". The total set of eigenstates can therefore be regarded as a complete orthogonal system; this means that the eigenvalue like the eigenfunctions, form an enumerable sequence.

Operators with an enumerable set of "discrete" eigenvalues are not the most general type associated with physical quantities; but the further discussion of their properties will lead quite naturally to the required generalization. If we expand the state vector f according to (1) in terms of the eigenfunctions of the operator A, we get for the expectation value of A in state f

---

* For such a treatment, see Von Neumann's treatise.

$$(Af, f) = \sum_i a_i \left|(f, \varphi_i)\right|^2$$

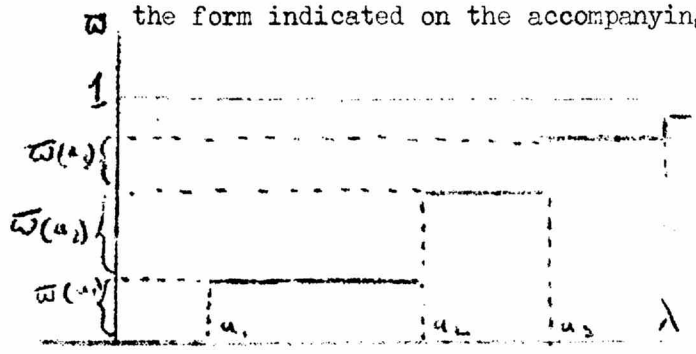
Assuming, for simplicity, all eigenvalues non-degenerate[*], this relation expresses the fact that the quahtity

$$\varpi(a_i; f) = \left|(f, \varphi_i)\right|^2$$

represents the probability of finding the eigenvalues a_i of A for a system in the state defined by f; one has, of course, the right normalization for probabilities $\sum_i \varpi(a_i; f) = 1$. For our class of operators with discrete eigenvalues, the statistical weights $\varpi(a_i; f)$ may be used to fix a measure in the sense of Stieltjes; i.e., we may write the expectation walue of A in the state f in the form of a Stieljes integral extended over the whole range of real values.

$$(Af, f) = \int_{-\infty}^{+\infty} \lambda \, d\varpi(\lambda; f) \qquad (3)$$

where the set function $\varpi(\lambda; f)$ is a discontinuous step function of the form indicated on the accompanying graph :



$$\varpi(\lambda, f) = \sum_{\text{all } a_i \le \lambda} \varpi(a_i; f) \qquad (4)$$

The interest of formula (3) is that it can be upheld with a determination of the measure $\varpi(\lambda; f)$ more general than that give by (4)

In order to arrive at this extension, we shall write formula (3) in a form in which the arbitrary state vector f does not appear explicitely. For this purpose, we associate with any state vector φ the <u>projection operator</u> P_φ defined by

$$P_\varphi f = (f, \varphi)\varphi \qquad (5)$$

With this notation, we may write, for any operator A with discrete eigenvalues

$$A = \sum_i a_i P_{\varphi_i} \qquad (6)$$

or, symbolically,

$$A = \int_{-\infty} \lambda \, d\, U(\lambda) \qquad (7)$$

---

[*] The way to take account of any degeracy is quite obvious. Our fundamental formulae (4) and (8) cover this caze as well.

with

$$U(\lambda) = \sum_{\text{all } a_i \leq \lambda} P_{\varphi_i} \qquad (8)$$

The meaning of the symbolical expressions (7) and (8) is given (3) and (4), we may say that for any state vector f, the measure $\omega(\lambda; f)$ is the expectation value of the operator $U(\lambda)$ in this state. The normalization relation may be written

$$\int_{-\infty}^{+\infty} \omega(\lambda; f) = 1,$$

or, in operator form, $$\int_{-\infty}^{+\infty} dU(\lambda) = 1$$

this explains the name "decomposition of unity" given by Von Neumann to the operator function $U(\lambda)$.

Now, decomposition of unity need not be restricted to the form (8), corresponding to discontinuous step functions of the type (4). We may have more general set functions $\omega(\lambda; f)$, e.g. continuous in some interval. In fact, the properties which entirely characterize a decomposition of unity completely are that the operator $U(\lambda)$ be Hermitian and idempotent (i.e. $U^2 = U$). According to (7), a given decomposition of unity completely defines an operator A; equation (7) expresses the "spectral decomposition" of A. The points of discontinuity of the decompostion of unity $U(\lambda)$ of A give discrete eigenvalues of A; intervals in which $U(\lambda)$ is continuous, but not constant, form the "continuous spectrum" of A. Not all Hermitian operators have a decomposition of unity; but it may be assumed that those operators which represent physical quantities belong to this class. We may then conclude that the decomposition of unity of the operator representing a physical quantity defines the probability distribution, for any state, of all the possible values of this quantity.

3.- Projection operators and traces. Projection operators may sometimes be used with advantage instead of the state vectors to which they belong. Thus, the expectation values of the quantity A in the state f may be expressed in terms of the projection operator P_f as

$$(Af, f) = \text{tr}\,(P_f A). \qquad (9)$$

The operation indicated by tr is taking the trace of the operator following it. If φ_i is any complete orthogonal system, the trace of the operator A is defined by :

$$\mathrm{tr}\, A = \sum_i (A\varphi_i, \varphi_i);$$

it is readily verified that this definition is independent of the choice of the sytem φ_i; The notation (φ) is especially convenient for expressing the distribution density of the values of an operator ; the probability of finding a value between λ and $\lambda + d\lambda$ when the system is in state f is

$$d\varpi(\lambda; f) = \mathrm{tr}\left[P_f\, d\,U(\lambda)\right] \qquad (10)$$

If the operator A has a degenerate eigenvalue a_i with a set of orthogonal eigenfunctions $\varphi_{i,m}$ the corresponding term in the spectral decomposition of A is $a_i U_i$ with

$$U_i = \sum_m P_{\varphi_{i,m}}$$

and the probability of finding this value in state f is accordingly $\mathrm{tr}\,(P_f U_i)$. Moreover, since $\mathrm{tr}\, P_f = 1$ for any normalised state vector $\mathrm{tr}\, U_1$ represents the degree of degeneracy of the eigenvalue a_i.

4.- Temporal evolution of a system. The way in which the state of a system varies in the course of time may be described by assigning the variation to the state vector. The fundamental equation of "motion" of a state vector ψ is

$$i\hbar \frac{\partial \psi}{\partial t} = H\psi, \qquad (11)$$

the operator H denoting the Hamiltonian of the system. In the representation thus adopted, which is called the " Schrödinger" representation the time variation is entirely ascribed to the state vectors, while the physical quantities are fixed operators in Hilbert space. This situation is quite analogous to usual onein classical theory ; the time dependent state vectors correspond to the classical trajectories; while the fixed operators correspond to the fixed phase functions which represent classical quantities. The time dependence of the latter is indirectly given by the variation of their argument, just as the time dependence of the expectation values of operators results from the variation of the

state vectors.

A further analogy with the classical case appears when the motion is regarded as a transformation of the state vector or the phase, respectively. The Schrödinger equation (11) defines an automorphism of Hilbert space just as the Hamiltonian equations define an automorphism of phase space. In Hilbert space, the canonical transformations are those which preserve the fundamental operation of scalar product of state vectors : they are the so-called unitary transformations. Now, equation (11) can be immediately integrated in operator form :

$$\psi(t) = e^{-\frac{i}{\hbar} H t} \psi(0) \qquad (12)$$

and this form shows explicitely the unitary transformation by which $\psi(0)$ is changed into $\psi(t)$. The corresponding transformation of the projection operators is

$$P_{\psi(t)} = e^{-\frac{i}{\hbar} H t} P_{\psi_0} e^{\frac{i}{\hbar} H t} ,$$

and the analogue of Liouville's theorem here reduces to the trivial statement of the invariance of the trace tr $P_{\psi(t)}$.

Chapter II.- THE ERGODIC THEOREM.

1.- The first ergodic theorem. The discussion of the equivalence between time averages and statistical averages in quantum theory is formally parallel to the classical one. It is still convenient to distinguish between strictly "isolated" systems, whose state is described at any time by the vector $\psi(t)$ arising from an initial one $\psi(0)$ by the undisturbed time evolution of the system, and systems whose initial state is more "coarsely" defined : there will correspond an ergodic theorem to each of these cases, like in classical theory.

From the point of view of the physical interpretation, however, the first isolated system of quantum theory is rather different from that of classical theory. While in the latter theory any initial phase fixes an energy surface in which the trajectory is entirely contained, an arbitrary chosen initial state vector $\psi(0)$ will in general define a statistical distribution of the system over all the possible values of the energy. The ergodic average of classical theory accordingly corresponds to detailed statistical distribution over all the phases of a definite energy surface; but there is no connexion between the distributions on different energy surfaces; the parallel ergodic theorem of quantum theory will give us a statistical distribution over all values of the energy, but without any reference to the distribution of other physical quantities. Such a difference clearly lies in the nature of the question. Although, as we shall see, it will be levelled out when the conditions of the second ergodic theorem are introduced, there nevertheless remains an important field of application for the first ergodic theorem ; we shall meet later with a specific example of such an application.

Let us consider the time evolution of an arbitrary state vector $\psi(0)$, as determined by the Schrodinger equation. We shall assume that the Hamiltonian H has only discrete eigenvalues E_i with eigenfunctions φ_i. We have initially a statistical distribution of the energy values :

$$\psi(0) = \sum_i (\psi(0), \varphi_i)\,\varphi_i ,$$

the coefficients $(\psi(0), \varphi_i)$ are complex numbers with definite amplitudes and phases :

$$(\psi(0), \varphi_i) = a_i\, e^{i\alpha_i}$$

At time t, the state vector has become

$$\psi(t) = \sum_i r_i e^{i\alpha_i} e^{-\frac{i}{\hbar}E_i t} \varphi_i ,$$

the probability density $\varpi(E_i;\psi) = r_i^2$ of the energy distribution is unchanged (this corresponds to the fixed energy surface of the classical case), but the phases vary with time.

The expectation value of the quantity A at time t may be written

$$(A\psi_t, \psi_t) = \sum_{i,k} r_i r_k e^{i(\alpha_i - \alpha_k)} (A\varphi_i, \varphi_k) e^{-\frac{i}{\hbar}(E_i - E_k)t}$$

It depends on the time only through the last exponential factor. Now, this factor has always an average value with respect to time : it is zero or one according as $E_i \neq E_k$ or $E_i = E_k$. Therefore, the time average $\overline{A}|_t$ of the expectation value $(A\psi_t, \psi_t)$ always exists; its character is essentially different, however, according as the eigenvalues of the energy are or are not degenerate. If there is no degeneracy, we have

$$\overline{A}|_t = \sum_i r_i^2 (A\varphi_i, \varphi_i) , \qquad (1)$$

if, on the other hand, to take a simple illustration, the two eigenvalues E_ℓ , E_m are equal, their contribution to the average $\overline{A}|_t$, besides the diagonal terms of the general type (1), will include a cross-term

$$2 r_\ell r_m \cdot \mathrm{Re}\left[e^{i(\alpha_\ell - \alpha_m)} (A\varphi_\ell, \varphi_m) \right]$$

(Re = real part of) depending on the initial phases α_ℓ, α_m.

We therefore see that in order ot obtain a time average of type (1), independent of the initial phases, we require an assumption about the eigenvalues of the energy, the absence of degeneracy : this assumption is the analogue of the classical hypothesis of the metrical indecomposability of the energy surface. Remembering the meaning of the coefficients r_i^2 and using the trace notation, we may write formula (1) in the form

$$\overline{A}|_t = \mathrm{Tr}(U_\psi A) , \qquad (2)$$

with

$$U_\psi = \sum \varpi(E_i, \psi) P_{\varphi_i} \qquad (3)$$

Formula (2) expresses the time average of A as a statistical average, which is the quantal analogue of the ergodic average defined by Birkhoff's therorem. The statistical operator U_ψ depends, as already explained, on ly on the probability density of the energy distribution in the initial state ψ, but not on the initial phases of the energy eigenfunctions in state ψ. As a matter of fact, the operator U_ψ simply results from averaging the projection operator P_ψ over these phases. Infact, from

$$P_\psi f = (f,\psi)\psi = \sum_{ik} \psi_i \psi_k e^{i(\alpha_i - \alpha_k)} (f,\varphi_k)\varphi_i$$

we get by averaging over the α's

$$\overline{P_\psi}_\alpha f = \sum_i |\psi_i|^2 P_{\varphi_i} f = U_\psi f$$

In other words, the time variation of the state vector has the effect in the long run, of uniformly distributing the initial phases over all possible values ; this somewhat loose statement is analogous to the classical picture of the trajectory "filling up" the energy surface. The averaging over the phases means that a "pure state", represented for the statistical purposes by a projection operator P_ψ is replaced by a statistical assembly, represented by the operator U_ψ.

2.- Macroscopic quantities and coarse distribution. As already pointed out, the statistical operator U_ψ only describes a distribution over the eigenvalues of the energy, without any further detail. If one tries in quantum theory to approximate the calssical description of the state of a system by a number of different physical quantities, one immediatly meats with the limitations in the assignment of definite values to such quantities which result from the non-commutability of the corresponding operators. A way out of this difficulty has been suggested by von Neumann*. The idea is to represent the macroscopic quantities by commutable operators constructed by an appropriate "smoothing out" procedure from those which give the idealized representation of the same quantities in a strict quantal description of the system.

Thus, the energy of the system is strictly represented by the Hamiltonian

$$H = \sum_i E_i P_{\varphi_i}$$

---

*J. Von Neumann, Z. Physik 57, 30, 1929.

we again assume the Hamiltonian to have only discrete eigenvalues. Let us now subdivide the energy-axis into a sequence of intervals I_a, each containing a certain number S_a of eigenvalues E_i; let us ascribe to each interval I_a a single value $\mathcal{E}_a$, which will be some average of the E_i's contained in I_a, and a projection operator

$$U_a \equiv U(I_a) = \sum_i^{(a)} P_{\varphi_i} \tag{4}$$

the summation $\sum^{(a)}$ extending to all eigenfunctions φ_i which pertain to the E_i's in I_a. We may then define a new operator $\mathcal{H}$, which we shall call the "macroscopic energy", by its spectral decomposition

$$\mathcal{H} = \sum_a \mathcal{E}_a U_a \tag{5}$$

We may describe this procedure as a "coarse" subdivision of the Hilbert space into energy shells, represented by the projection operators U_a. To each shell corresponds a degenerate value of the 'macroscopic' energy, of degree of degeneracy $S_a = \mathrm{tr}\, U_a$.

Any other macroscopic quantity A must commute with the macroscopic energy $\mathcal{H}$: its eigenfuncrions ω_k are therefore linearly related to the φ_i's. In particular, one may re-write formula (4) in terms of the P_{ω_k}:

$$U_a = \sum_k^{(a)} P_{\omega_k} \tag{6}$$

the summation extends over all the P_{ω_k} belonging to the interval I_a. Now, it may happen that the ω_k's belonging to I_a correspond to several distinct eigenvalues of A: in this case, such eigenvalues will characterize a certain subdivision of the interval I_a into smaller intervals i_a, i.e. of the energy shell U_a into cells

$$u_a^{(\nu)} = \sum_k^{(a,\nu)} P_{\omega_k} \tag{7}$$

(the summation extends over all the P_{ω_k}'s belonging to the interval $i_a^{(\nu)}$ of degeneracy $s_a^{(\nu)} = \mathrm{tr}\, u_a^{(\nu)}$).

By using a sufficient number of suitable macroscopic quantities $A, B, C, \ldots$ one finally arrives at a subdivision of each energy shell U_a into N_a cells of type (7), in such a way that *

$$U_a = \sum_{\nu=1}^{N_a} u_a^{(\nu)} \quad ; \quad S_a = \sum_{\nu=1}^{N_a} s_a^{(\nu)} \tag{8}$$

* We take the ω_k's to be the set of eigenfunctions common to all the macroscopic variables considered.

We shall not here raise the question whether this cell subdivision can actually be brought down to limits sufficiently near to these imposed by the uncertainty relations; von Neumann has shown that it is indeed possible to construct a set of "macroscopic" coordinates and momenta Q_k, P_k satisfactory in this respect. All macroscopic quantities of physical interest can then be expressed as functions $f(Q_k, P_k)$.

3.- Von Neumann's ergodic theorem. The coarse cell distribution in Hilbert space just defined forms the basis for the formulation of a second ergodic theorem, due to Von Neumann, and widely analogous to the classical ergodic theorem of Hopf. We envisage a macroscopic quantity

$$A = \sum_a \sum_{\nu=1}^{N_a} a_a^{(\nu)} u_a^{(\nu)}$$

and its expectation value in any state $\psi(t)$ at time t :

$$A(\psi_t) = tr(P_{\psi_t} A) = \sum_a \sum_{\nu=1}^{N_a} a_a^{(\nu)} w_a^{(\nu)}(t) \qquad (9)$$

$$w_a^{\nu}(t) = tr(P_{\psi_t} u_a^{(\nu)})$$

The statement of Von Neumann's ergodic theorem is that there exists a statistic l average $\overline{A}|_\psi$ equivalent to the time average of $A(\psi_t)$ in as much as the mean quadratic fluctuation

$$\frac{1}{T}\int_0^T |A(\psi_t) - \overline{A}|_\psi|^2 dt \qquad (10)$$

tends to zero in the sense of probability, provided that certain conditions (which we shall formulate in the course of the analysis) are fulfilled by the system. Convergence "in the sense of probability" means that the probability that the quantity in question does not tend to zero can be made as small as one likes.

The expression for the statistical average $\overline{A}|_\psi$ is a direct extension to our coarse distribution of that given by the first ergodic theorem

$$\overline{A}|_\psi = tr(U_\psi A)$$

$$U_\psi = \sum_a \frac{tr(P_{\psi_0} U_a)}{tr\, U_a} U_a \qquad (11)$$

In fact, by Chapter I, §3, the quantity $W_a = tr(P_{\psi_0} U_a)$ is the total probability for the initial state ψ_0 of finding the

macroscopic energy in the interval I_a (i.e. with the value $\mathcal{E}_a^{(\varrho)}$), and $\mathrm{tr}[U_a]^{-1} U_a = U_a / S_a$ is the mean projection operator in this interval. With the notation introduced so far, we can write (11) as

$$\mathcal{A}|\psi = \sum_a \sum_{\nu=1}^{N_a} a_a^{(\nu)} s_a^{(\nu)} \frac{W_a}{S_a} \tag{12}$$

The form of the expression

$$|\mathcal{A}(\psi_t) - \mathcal{A}|\psi|^2 = \left| \sum_a \sum_\nu a_a^{(\nu)} \left[w_a^{(\nu)} - \frac{s_a^{(\nu)} W_a}{S_a} \right] \right|^2$$

suggests a comparison with the average of the quantity A^2

$$\overline{\mathcal{A}^2}|\psi = \sum_a \sum_\nu (a_a^{(\nu)})^2 s_a^{(\nu)} \frac{W_a}{S_a}$$

By an application of Schwarz's inequality we indeed find

$$|\mathcal{A}(\psi_t) - \overline{\mathcal{A}}|\psi|^2 \leqslant \overline{\mathcal{A}^2}|\psi \sum_a \sum_\nu \frac{S_a}{s_a^{(\nu)} W_a} \left(w_a^{(\nu)} - \frac{s_a^{(\nu)} W_a}{S_a} \right)^2$$

We shall have proved the theorem if we show that the factor of $\overline{\mathcal{A}^2}|\psi$ in the right hand side of this inequality, after time averaging, tends to zero in the sense of probability.

The only quantity depending on thetime is

$$w_a^{(\nu)}(t) = \sum_k^{(a,\nu)} |(\psi_t, \omega_k)|^2$$

For ψ_t we may write, using the same notation as in § 1,

$$\psi_t = \sum_i r_i e^{i\beta_i} \varphi_i \,, \quad \beta_i = \alpha_i - \frac{1}{\hbar} E_i t$$

We thus have

$$w_a^{(\nu)}(t) = \sum_k^{(a,\nu)} \left| \sum_i r_i e^{i\beta_i} (\varphi_i, \omega_k) \right|^2$$

$$= \sum_{i,j}^{(a)} r_i r_j e^{i(\beta_i - \beta_j)} C_{ij}^{(a,\nu)}$$

with

$$C_{ij}^{(a,\nu)} = \sum_k^{(a,\nu)} (\varphi_i, \omega_k)(\omega_k, \varphi_j) \tag{13}$$

The $C_{ij}^{(a,\nu)}$ thus defined obviously vanish unless φ_i φ_j both belong to the interval I_a; hence the restriction of the summation over i, j, to this interval. Moreover, if φ_i, φ_j belong to I_a,

$$\sum_{\nu=1}^{N_a} C_{ij}^{(a\nu)} = \delta_{ij}$$

and therefore $$W_a = \sum_{\nu=1}^{N_a} w_a^{(\nu)}(0) = \sum_i^{(a)} r_i^2 \qquad (14)$$

We thus have to take the time average of quantities of the form

$$\chi_a^{(\nu)} \equiv \left(w_a^{(\nu)} - \frac{s_a^{(\nu)} W_a}{S_a} \right)^2 = \left\{ \sum_{ij}^{(a)} r_i r_j e^{i(\beta_i - \beta_j)} \left[C_{ij}^{(a,\nu)} - \frac{s_a^{(\nu)}}{S_a} \delta_{ij} \right] \right\}^2$$

We see that these time averages reduce to expressions independent of the phases α_i, α_j only if the two following conditions aresatisfied :

a) no eigenvalue E_i of the Hamiltonian H is degenerate,

b) there are no energy "resonances", i.e. no two energy differences $E_i - E_j$ are equal. Note here again the parallelism with the conditions of validity of Hopf's ergodic theorem : besides the metrical indecomposability of each energy surface (corresponding to condition a), we had to assume metrical indecomposability for almost energy surfaces in the product space, which is analogous to our present condition (b). Under conditions (a) and (b), we get for the time average of $\chi_a^{(\nu)}$ the expression

$$\overline{\chi_a^{(\nu)}} = \left\{ \sum_i^{(a)} r_i^2 \left[C_{ii}^{(a,\nu)} - \frac{s_a^{(\nu)}}{S_a} \right] \right\}^2 + \sum_{i \neq j}^{(a)} r_i^2 r_j^2 \left| C_{ij}^{(a,\nu)} \right|^2$$

Applying Schwarz's inequality to the first term and using (14) we have

$$\overline{\chi_a^{(\nu)}} \leqslant W_a \sum_i^{(a)} r_i^2 \left[C_{ii} - \frac{s_a^{(\nu)}}{S_a} \right]^2 + \sum_{i \neq j}^{(a)} r_i^2 r_j^2 \left| C_{ij}^{(a,\nu)} \right|^2$$

and accordingly

$$\sum_a \sum_{\nu=1}^{N_a} \frac{S_a}{s_a^{(\nu)} W_a} \overline{\chi_a^{(\nu)}} \leqslant \sum_a \left\{ \sum_i^{(a)} r_i^2 M_{ii}^{(a)} + \sum_{i \neq j}^{(a)} \frac{r_i^2 r_j^2}{W_a} M_{ij}^{(a)} \right\} \qquad (15)$$

where

$$M_{ij}^{(a)} = \sum_{\nu=1}^{N_a} \frac{S_a}{s_a^{(\nu)}} \left| C_{ij}^{(a,\nu)} - \frac{s_a^{(\nu)}}{S_a} \delta_{ij} \right|^2 \qquad (16)$$

In the expression on the right hand side of (15), the factors which depend on the state vector considered, viz. the r_i's and W_a, are separated from the coefficients $M_{ij}^{(a)}$, in which the influence of the coarse subdivision of the Hilbert space into cells is concentrated. It is clear that the right hand side of (15) will always be $\leqslant 2\xi \sum W_a$, i.e. $\leqslant 2\xi$ for any state vector, provided only that all $M_{ij}^{(a)}$ are themselves $\leqslant \xi$. The crucial step in the proof of the ergodic theorem is the study of the distribution of the values of the $M_{ij}^{(a)}$'s for all

possible cell subdivisions. This will lead to an estimate of the probability that the parameter ξ be larger than any given value ξ_0 and will show under which condition this probability can be sufficiently reduced.

Von Neumann's original argument has been simplified and sharpened by Pauli and Fierz*, to whose paper we refer the reader for all details. The starting point is the obserbation that the (φ_i, ω_k) which enter into the expression for the $C_{ij}^{(a\nu)}$ can be regarded, for any interval I_a, as defining a set of S_a orthogonal unit vectors in a complexe space of S_a dimensions; each $C_{ij}^{(a\nu)}$ represents the scalar product of the projections of two such vectors on a $\delta_a^{(\nu)}$ of $\delta_a^{(\nu)}$ dimensions. With the help of this geometrical model, the "moments" of the distribution of the M_{ij}, i.e. the average values of the various powers $\left[M_{ij}^{(a)}\right]^n$ taken over all possible orientations of the vector set just described, can be valuated. From the moments, an estimate of the probability distribution readily follows.

The probability that, for any interval I_a, the upper bound of the $M_{ij}^{(a)}$ be larger than ξ_0 is found to be of the form

$$\text{const } e^{-b\sqrt{\frac{S_a}{N_a}}\xi_0 + 2\log S_a} \qquad (17)$$

where b is a number of the order of unity; this estimate is valid for $\xi_0 > \frac{2N_a}{S_a - 2}$. We this see that for not too small values of ξ_0, the probability (17) becomes vanishingly small provided only that

$$\frac{S_a}{N_a} \gg (2\log S_a)^2$$

This is the essential condition to be fulfilled by our coarse cell subdivision of the Hilbert space in order to ensure the validity of the ergodic theorem. It means that the average number of eigenfunctions in any coarse cell must be large : a quite reasonable requirement.

It must be admitted that von Neumann's ergodic theorem looks rather forbiffing and ill-suited to practical applications. Fortunately, as we shall see, its use is not required for the solution of actual physical problems. It has essentially the character of an existence theorem, by means of which statistical distributions more nearly approximating situations of physical interest can be derived. Thus, we shall presently see, in the next chapter, how von Neumann's theorem supplies the basis for distribution, which describes the statistical behaviour of systems of definite temperature.

* W. Pauli and M. Fierz, Z. Physik 106, 572, 1937.

Chapter III.- STATISTICS OF CLOSED SYSTEMS.

1.- Statistics of composite systems. The course we shall follow from now on will be closely parallel to the development of the calssical theory : we shall study successively closed systems in thermal contact with their surroundings and open systems , and in each case the argument will be essentially the same as in classical theory : only the formal aspect will undergo the changes required by the quantal mode of description. Thus, for the discussion of a closed system in contact with a thermostat we first need a formal treatment of composite systems, whose various parts are assumed to be in weak interaction with each other.

Let us consider, e.g., two systems, each described in its own Hilbert space by the Hamiltonian $H^{(1)}$, $H^{(2)}$ and state vectors $\psi^{(1)}$, $\psi^{(2)}$. The composite system resulting from the juxtaposition of these two systems is described in a Hilbert space which is the direct product of the two individual spaces. Its Hamiltonian is

$$H = H^{(1)} \times 1^{(2)} + H^{(2)} \times 1^{(1)},$$

where $1^{(k)}$ denotes the unit operator in the Hilbert space of system (k) and the cross indicates the direct product of operators pertaining to different Hilbert spaces. The state vectors of the composite system are products $\psi^{(1)} \times \psi^{(2)}$ and the corresponding projection operators direct products $P^{(1)} \times P^{(2)}$. The operator which governs the statistical behaviours of the composite system is the decomposition of unity of the Hamiltonian : this is we must try to determine.

Let $E_i^{(k)}$, $\varphi_i^{(k)}$ be the eigenvalues and eigenfunctions of the Hamiltonian $H^{(k)}$, and $P_{\varphi_i}(k)$ the projection operator of $\varphi_i^{(k)}$ in the Hilbert space of system (k). The energy eigenvalues of the total system will be of types $E_i^{(1)} + E_j^{(2)}$ with corresponding projection operators $P_{\varphi_i}(1) \times P_{\varphi_j}(2)$ (or sums of such operator products if there is degeneracy). In particular, the projection operator $U(I)$ belonging to an interval I of possible values of the total energy will be a sum

$$U(I) = \sum_{(I)} P_{\varphi_i}(1) \times P_{\varphi_j}(2)$$

extended over all pairs $\varphi_i^{(1)}$, $\varphi_j^{(2)}$ belonging to eigenvalues $E_i^{(1)} + E_j^{(2)}$ contained in I. Quite generally, therefore, the decomposition of unity

of the total energy is

$$dU(\lambda) = \int_{-\infty}^{\infty} dU^{(1)}(\lambda') \cdot dU^{(2)}(\lambda - \lambda')$$

where $dU^{(k)}(\lambda)$ represents the decomposition of unity of the Hamiltonian $H^{(k)}$, and the integration is performed with respect to λ'.

The expression for $dU(\lambda)$ is immediately generalised to a system composed of N parts with additive Hamiltonian

$$H = \sum_k 1^{(1)} \times 1^{(2)} \times \ldots \times H^{(k)} \times \ldots \times 1^{(N)}.$$

The decomposition of unity of this operator is

$$dU(\lambda) = \iint\cdots\int_{(\lambda_1, \lambda_2, \ldots \lambda_N)} dU^{(1)}(\lambda_1) \times dU^{(2)}(\lambda_2) \times \ldots \times dU^{(N-1)}(\lambda_{N-1}) \times dU^{(N)}\left(\lambda - \sum_{k=1}^{N-1} \lambda_k\right) \quad (1)$$

From this formula we derive a "law of decomposition" for the traces*:

$$tr[dU(\lambda)] = \iint\cdots\int_{(\lambda_1, \lambda_2, \ldots \lambda_{N-1})} \prod_{k=1}^{N-1} tr[dU^{(k)}(\lambda_k)] \cdot tr\left[dU^{(N)}\left(\lambda - \sum_{k=1}^{N-1} \lambda_k\right)\right] \quad (2)$$

which is entirely analogous to the law of composition of the invariant measures of energy surfaces in the classical case (Part I, Ch. III, §2). In fact, at this point, Khinchin's argument can be taken up again and repeated without essential modification.

For each component of the system, we associate with the "weight" $tr\left[dU^{(k)}(\lambda)\right]$ of the energy interval $(\lambda, \lambda + d\lambda)$ normalized probability distribution (in the sense of a Stieltjes measure)

$$d\varpi^{(k)}(\lambda) = \frac{e^{-\beta\lambda}\, tr\left[dU^{(k)}(\lambda)\right]}{Z^{(k)}(\beta)} \quad (3)$$

which satisfies a law of composition of the same form as (2). The normalization factor is

$$Z^{(k)}(\beta) = \int_{-\infty}^{\infty} e^{-\beta\lambda} tr\left[dU^{(k)}(\lambda)\right] = tr\left[e^{-\beta H^{(k)}}\right], \quad (4)$$

If the total system has a large number of components, we get for its probability distribution the asymptotic expression

$$d\varpi(\lambda) \simeq \frac{1}{\sqrt{2\pi B}} e^{-\frac{(\lambda - \bar{E})^2}{2B}} d\lambda, \quad (5)$$

where

---

* We use the same symbol tr to indicate the trace taken in any one of our Hilbert spaces.

$$\bar{E} = \sum_k \bar{E}^{(k)}, \quad \bar{E}^{(k)} = \frac{1}{Z^{(k)}(\beta)} \int_{-\infty}^{+\infty} \lambda e^{-\beta\lambda} \, tr\left[dU^{(k)}(\lambda)\right] = -\frac{d}{d\beta} \log Z^{(k)}(\beta) \quad (6)$$

represents the average value of the energy in this distribution, and

$$B = \sum_k \ell^{(k)}, \quad \ell^{(k)} = \frac{1}{Z^{(k)}(\beta)} \int_{-\infty}^{+\infty} (\lambda - \bar{E}^{(k)})^2 e^{-\beta\lambda} \, tr\left[dU^{(k)}(\lambda)\right] = \frac{d^2}{d\beta^2} \log Z^{(k)}(\beta) \quad (7)$$

is the sum of the mean squafe fluctuations of the energies of the components.

2.- The canonical distribution. We can now be very brief in establishing the canonical distribution law in its quantal form for a systen S in contact with a thermostat T, for the argument is little else than a repetition of the classical one. To the total system $\mathfrak{S}$ we apply Von Neumann's ergodic operator $\mathcal{U}_\psi$. For the initial state ψ in which we consider the system $\mathcal{S}$, we may choose an eigenstate of its energy. This reduces essentially to the projection operator U_a belonging to the interval I_a in which the corresponding eigenvalue λ is contained; this projection operator will be more conveniently denoted by $\Delta U(\lambda)$, and

$$\mathcal{U}_\psi = \frac{\Delta U(\lambda)}{tr\left[\Delta U(\lambda)\right]} .$$

Now, assuming a weak interaction between system and thermostat, we may write

$$dU(\lambda) = \int dU_S(\lambda') \times dU_T(\lambda - \lambda') \quad ;$$

and in particular,

$$\Delta U(\lambda) = \int dU_S(\lambda') \times \Delta U_T(\lambda - \lambda') \quad ;$$

i.e. the "coarseness" of the energy definition of the total system is entirely referred to the thermostat; it does not affect at all the energy λ' of the system S, for which we shall obtain a "fine" distribution.

In fact, any operator A_S pertaining to the system S gives rise to an operator in a special form in the Hilbert space of the total system, viz.

$$A = A_S \times 1_T,$$

whose average is given by

$$\bar{A}_S = tr(\mathcal{U}_\psi A) = \int tr\left[A_S \, dU_S(\lambda')\right] \frac{tr \, \Delta U_T(\lambda - \lambda')}{tr \, \Delta U(\lambda)}$$

For both the thermostat and the total system we may use the asymptotic form (5) of the distribution law, and we may treat the energy interval $\Delta\lambda$ defining the thickness of the energy shell as a "physically infinitesimal" quantity. We then get in excatly the same way as in the classical case

$$\frac{tr[\Delta U_T (\Lambda-\lambda')]}{tr(\Delta U(\lambda))} \simeq \frac{1}{Z_S(\beta)} e^{-\beta\lambda'}$$

The statistical operator of the canonical distribution is thus

$$U_\beta = \frac{1}{Z_S(\beta)} \int e^{-\beta\lambda'} d U_S(\lambda')$$

i.e. (dropping the index S)

$$U_\beta = \frac{1}{Z(\beta)} e^{-\beta H}, \text{ with } Z(\beta) = tr[e^{-\beta H}]; \qquad (8)$$

in this formula H is the Hamiltonian of the system and β the inverse of the absolute temperature ; it is uniquely related to the average energy of of the thermostat by the equation

$$-\frac{d}{d\beta} \log Z_T(\beta) = \bar{E}_T$$

The canonical average of any quantity is expressed by means of the operator U_β in the form

$$\bar{A} = tr(U_\beta A). \qquad (9)$$

The statistical interpretation of thermodynamics can simply be taken over from the classical theory. The free energy is $F = -\theta \log Z(\beta)$ and the entropy can be put in the form

$$S = -tr[U_\beta \log U_\beta] \qquad (10)$$

One point, however, requires special consideration : it is the proof of the permanence of the canonical distribution during quasi-static adiabatic transformations.

4.- Quasi-static adiabatic transformations. Let us start from a system of given temperature, with the statistical operator

$$U_{\beta_0} = \frac{e^{-\beta_0 H(a_0)}}{tr[e^{-\beta_0 H(a_0)}]}$$

We assume the Hamiltonian $H(a)$ to have, for any value of the external parameter a, discrete and non-degenerate eigenvalues $E_i(a)$ with eigen-

functions $E_i(a)$. If after breaking the contact with the thermostat, we suddenly change the external parameter from a_o to $a = a_o + d_a$, each of the state vectors $\varphi_i(a_o)$ will evolve according to the Schrödinger equation pertaining to the new Hamiltonina H(a). According to the first ergodic theorem*, the statistical operator $P_{i}(a_o)$ corresponding to this state vector will eventually take the equilibrium form

$$\sum_{i} tr\left(P_{\varphi_i(a_o)} P_{\varphi_j(a)}\right) P_{\varphi_j(a)}$$

But the state vector $\varphi_i(a_o)$ was initially represented in the statistical operator U_{β_o} by its projection operator $P_{\varphi_i(a_o)}$ with the coefficient $\frac{1}{Z(\beta_o, a_o)} e^{-\beta_o E_i(a_o)}$. The statistical operator corresponding to the new equilibrium is therefore

$$U(a) = \frac{1}{Z(\beta_o, a_o)} \sum_{i,j} e^{-\beta_o E_i(a_o)} tr\left(P_{\varphi_i(a_o)} P_{\varphi_j(a)}\right) P_{\varphi_j(a)}$$

$$= \frac{\sum_{i} tr\left[e^{-\beta_o H(a_o)} P_{\varphi_i(a)}\right] P_{\varphi_j(a)}}{tr\left[e^{-\beta H(a_o)}\right]} \quad . \qquad (11)$$

We have now to evaluate the traces occuring in the expression (11) for $U(a)$ in terms of the new Hamiltonian; i.e. we must substitute for $H(a_o)$ its value in terms of H(a) :

$$H(a_o) = H(a\ ) - da \frac{\partial H}{\partial a} .$$

This calculation demands some care, because the two terms in the expression for $H(a_o)$ do not generally commute. Since we only require a result accurate to the first order in da, we may write

$$e^{-\beta_o\left[H(a) - da \frac{\partial H}{\partial a}\right]} = e^{-\beta_o H(a)} + \beta_o da \sum_{n=0}^{\infty} \frac{1}{n!} (-\beta)^{n-1} \sum_{m=0}^{n-1} H^m \frac{\partial H}{\partial a} H^{n-1-m} ;$$

but $\left(\sum_{m=0}^{n-1} H^m \frac{\partial H}{\partial a} H^{n-1-m} \varphi_j, \varphi_j\right) = n E_j^{n-1} \left(\frac{\partial H}{\partial a} \varphi_i, \varphi_j\right),$

---

* There is no question of introducing here any coarse energy shells, and applying Von Neumann's ergodic theorem, as L. Broer erroneously tried to do in his Amsterdam thesis (1945). As already emphasized, we are here dealing with a fine distribution of our system because we consider it initially in contact with its surroundings.

and therefore

$$\left(e^{-\beta_0 H(a_0)}\varphi_j(a), \varphi_j(a)\right) = e^{-\beta_0 E_j(a)}\left[1+\beta_0 da\, \overline{A}\right]_{E_j}$$

with the notation $$\overline{A}\Big]_{E_j} = \left(\frac{\partial H}{\partial a}\varphi_j, \varphi_j\right)$$

for the expectation value of the force in the state $\varphi_j(a)$. For the denominator of (11) we thus have

$$\mathrm{tr}\left[e^{-\beta_0 H(a_0)}\right] = \sum_j e^{-\beta_0 H(a)}\left[1+\beta_0\, da\, \overline{A}\Big]_{E_j}\right]$$

$$= \mathrm{tr}\left[e^{-\beta_0 H(a)}\right]\cdot\left[1+\beta_0\, da\cdot\bar{A}\right],$$

where $\bar{A}$ denotes the canonical average of the force for the values β_0, a of the thermodynamical variables. The operator (11) accordingly takes the form

$$U(a) = \frac{1}{\mathrm{tr}\left[e^{-\beta_0 H(a)}\right]}\, e^{-\beta_0 H(a)}\left\{1-\beta_0\, da\left[\bar{A}-\overline{A}\right]\right\}$$

We may write this more compactly by introducing the operator

$$\overline{A}\Big] = \sum_j \overline{A}\Big]_{E_j}\, P_{\varphi_j},$$

which commutes with the Hamiltonian H(a). Therefore,

$$U(a) = \frac{1}{\mathrm{tr}\left[e^{-\beta_0 H(a)}\right]}\, e^{-\beta_0 H(a)}\left\{1-\beta_0\, da\left[\bar{A}-\overline{A}\Big]\right]\right\}$$

The operator $\overline{A}\Big]$, commuting with H, can be regarded as a function of H; let us assume that it can be expanded in the neighbourhood of the value A_E that it takes when H is replaced by its canonical average E :

$$\overline{A}\Big] = \overline{A}\Big]_{\bar{E}} + \left(\frac{\partial \overline{A}\Big]}{\partial H}\right)_{\bar{E}}(H-\bar{E}) + \frac{1}{2}\left(\frac{\partial^2 \overline{A}\Big]}{\partial H^2}\right)_{\bar{E}}(H-\bar{E})^2 + \ldots.$$

Taking the canonical average, we get for $\bar{A}$ the similar expansion :

$$A = \overline{A}\Big]_{\bar{E}} + \qquad\qquad + \frac{1}{2}\left(\frac{\partial^2 \overline{A}\Big]}{\partial H^2}\right)_{\bar{E}}\overline{(H-\bar{E})^2} + \ldots.$$

By the same argument as in the classical case, we can show that the difference $\overline{A}\Big] - \bar{A}$ is equal to $\left(\frac{\partial \overline{A}\Big]}{\partial H}\right)_{\bar{E}}(H-\bar{E})$ except for terms at most of the order of relative fluctuations which are negligible for macros-

copic systems. Now, a change of modulus in the statistical operator

$$U_{\beta_0}(a) = \frac{e^{-\beta_0 H(a)}}{tr\left[e^{-\beta_0 H(a)}\right]}$$

yields

$$U_{\beta_0}(a) = U_{\beta}(a)\left[1 + d\beta\, H - \bar{E}\right]$$

We thus see that the new statistical operator $U(a)$ has approximately the canonical form $U_{\beta}(a)$ provided that the variation $d\beta$ of modulus is connected with the variation of external parameter da by the relation

$$d\beta + \beta_0\, da \left(\frac{\partial \lambda}{\partial H}\right)_{\bar{E}} = 0,$$

whose thermodynamical interpretation is the classical one.

5.- Irreversible transformations. Gibbs' classical treatment of irreversible transformations can be readily transposed to quantum theory* We consider arbitrary statistical operators U or rather, following Gibbs' example, the corresponding probability exponents η, defined by $U = e^{\eta}$ We have then to compare the average probability exponents $tr(\eta e^{\eta})$ under various conditions.

(a) Adiabatic transformations : As we have just seen, if we start from a statistical distribution of the form $e^{\eta} = \sum_k e^{\eta_k} P_{\varphi_k}$ and perform a small change of the external parameters; we arrive eventually at a distribution

$$e^{\eta^{(1)}} = \sum_i e^{\eta_i^{(1)}} P_{\varphi_i^{(1)}},$$

whose density fulfils the condition

$$e^{\eta_i^{(1)}} = tr\left(e^{\eta} P_{\varphi_i^{(1)}}\right) = \sum_k e^{\eta_k} w_{ki}, \qquad (12)$$

with

$$w_{ki} = \left|(\varphi_k, \varphi_i^{(1)})\right|^2;$$

we have

$$\sum_i w_{ki} = \sum_k w_{ki} = 1. \qquad (13)$$

This is the analogue of the condition of Gibbs' first lemma. We accordingly prove that under condition (12)

$$tr\left(\eta^{(1)} e^{\eta^{(1)}}\right) \leq tr\left(\eta e^{\eta}\right). \qquad (14)$$

In fact, using the relation (12)

---

* O. Klein, Z. Physik 72, 767, 1931.

$$\mathrm{tr}(\eta e^{\eta}) - \mathrm{tr}\,(\eta^{(0)} e^{\eta^{(0)}}) = \sum_k e^{\eta_k} \{\eta_k - \sum_i \eta_i^{(0)} w_{ki}\},$$

or, by (13),

$$= \sum_{i,k} e^{\eta_k} w_{ki} (\eta_k - \eta_i^{(0)}) \quad . \tag{15}$$

On the other hand, again using (13), the normalization conditions $\mathrm{tr}(e^{\eta}) = \mathrm{tr}\,(e^{\eta^{(0)}}) = 1$ may be written

$$\sum_{i,k} e^{\eta_k} w_{ki} = \sum e^{\eta_i^{(0)}} w_{ki} = 1 ,$$

whence

$$\sum_{i,k} e^{\eta_k} w_{ki} \left(e^{\eta_i^{(0)} - \eta_k} - 1\right) = 0$$

Addingt this to the right hand side of (15) gives (14) in virtue of the identity $e^x - 1 - x \geq 0$. The discussion of adiabatic transformations on the basis of the inequality (14) is the same as in classical theory.

(b) Heat exchange. The theory of heat exchange is likewise contained in the analogue of Gibbs' second lemma : if a system is composed of two parts in weak interaction, any statistical distribution e^{η} pertaining to it has a spectral decomposition of the form

$$e^{\eta} = \sum_{i,k} e^{\eta_{ik}} P_{\varphi_i^{(1)}} \times P_{\varphi_k^{(2)}}$$

and defines the statistical operators $e^{\eta^{(1)}}$, $e^{\eta^{(2)}}$ for the component systems by

$$e^{\eta^{(1)}} = \sum e^{\eta_i^{(1)}} P_{\varphi_i^{(1)}} , \quad e^{\eta^{(2)}} = \sum_k e^{\eta_k^{(2)}} P_{\varphi_k^{(2)}}$$

with

$$e^{\eta_i^{(1)}} = \sum_k e^{\eta_{ik}} \quad , \quad e^{\eta_k^{(2)}} = \sum_i e^{\eta_{ik}} \tag{16}$$

We then have

$$\mathrm{tr}\,(\eta e^{\eta}) \geq \mathrm{tr}\,(\eta^{(1)} e^{\eta^{(1)}}) + \mathrm{tr}\,(\eta^{(2)} e^{\eta^{(2)}}) \tag{17}$$

The proof is immediate : we have, with (16),

$$\mathrm{tr}(\eta e^{\eta}) - \mathrm{tr}(\eta^{(1)} e^{\eta^{(1)}}) - \mathrm{tr}(\eta^{(2)} e^{\eta^{(2)}}) = \sum_{i,k} e^{\eta_{ik}} (\eta_{ik} - \eta_i^{(1)} - \eta_k^{(2)})$$

whence (17) follows.

It is not necessary to pursue this kind of considerations any further : the parallelism with Gibbs' classical discussion is quite obvious. There is, however, in quantum theory, a kind of irreversible process which does not occur for classical systems : a measurement per-

formed on a quantal system produces in general an irreversible change of the state of the system: it is interesting to investigate the accompanying increase of entropy.

6.- The process of measurement.* If we have a system in a "pure" state ψ, its statistical operator is represented by the projection operator P_ψ : strictly speaking, there is no thermodynamical analogy to this case, just as little as to the case of a classical mechanical system on a definite trajectory. The statistics of the pure state is a fundamental property of quantal systems, which has nothing to do with thenodynamics. As we have seen, the quantal model of a macroscopic situation, to which thermodynamics can be applied, involves an element of "coarseness", expressed by the change from the operator P_ψ to the statistical operator

$$\sum_{a,\nu} \frac{tr(P_\psi u_a^{(\nu)})}{tr\, u_a^{(\nu)}}\, u_a^{(\nu)}$$

This corresponds to passing from a single classical trajectory to a "tube of flow" in phase space, composing all trajectories defined by the phases of a finite cell.

However, the fact that a quantal system even in a well-defined state involves a statistical distribution has in one respect consequences of the same general kind as the effects considered in thermodynamics : a measurement performed on such a quantal system is a macroscopic process by which the "pure state" is transformed into a "mixture" of all the eigenstates of the quantity measured. The question therefore arises wether the entropy concept can be extended so as to apply to this specifically quantal type of irreversible transformation. The answer given by Von Neumann to this question is extremely simple: if a quantal system in is a state represented by the statistical operator U, its entropy may be defined as

$$S(U) = - \mathrm{tr}\,[U \log U] \qquad (18)$$

This expression vanishes for any pure state, for which U is of the form P_ψ. In order to check the adequacy of the definition (18), we must therefore show, in the first place, that any two pure states of a quantal system have the same entropy in the sense of thermodynamics

---

* J. Von Neumann, Gottingen Nachrichten 1927, p. 273

i.e; that it is possible to pass from any pure state to any other by a quasi-static transformation which does not involve any heat exchange. This seems at first sight somewhat surprising, especially if the two states ψ, φ are orthogo ln, since in that case no direct measurement performed on the system in state ψ will ever yield state φ. But as we shall see, the quasi-static transition from the one to the other be omes possible if we use an a propriate sequence of intermediate steps. It will suffice to discuss the case of two orthogoanl states, since any two others can be linked together by a third one, orthogonal to both of them.

Let us consider the sequence of $(p + 1)$ states defin ed by

$$\psi_r = \cos \frac{\pi r}{2p} \cdot \psi + \sin \frac{\pi r}{2p} \varphi , \quad = 0, 1, 2, \ldots, p; \qquad (19)$$

the first state ψ_0 is our initial state ψ, the last one ψ_p our final state φ, orthogonal to ψ. We start from an assembly of copies of the system considered all in state ψ_0. If we perform on all these sys tems the measurement of some quantity A_1 which has ψ_1 as one of its eigenfunctions, we transform the original assembly into a mixture, a fraction $|(\psi_0, \psi_1)|^2 = \cos^2 \frac{\pi}{2p}$ of which is in state ψ_1. Next we measure a quantity A_2, having ψ_2 as oneof its eigenfunctions; the new mixture resulting from this measurement contains a fonction ϖ_2 of systems in state ψ_2 which is at least the fraction of states ψ_2 contained in the state ψ_1; i.e.

$$\varpi_2 \geq |(\psi_0, \psi_1)|^2 \cdot |(\psi_1, \psi_2)|^2;$$

but from (19) we get quite generally

$$|(\psi_1, \psi_2)|^2 = |(\psi_r, \psi_{r+1})|^2 = \cos^2 \frac{\pi}{2p} .$$

Therefore, $\varpi_2 \geq \cos^4 \frac{\pi}{2p}$. Proceeding in the sale way, we finally arrive at a mixture containing a fraction ϖ_p of sysyems in state ψ_p for which we may write

$$\varpi_p \geq \cos^{2p} \frac{\pi}{2p}$$

Since $\lim_{p \to \infty} \cos^{2p} \frac{\pi}{2p} = 1$, we see that by taking q sufficiently large number of intermediate steps, we can actua ly transform the assembly in the pure state ψ into an assembly in the pure state φ. Moreover,

the operations invoved in the sequence of measurements do not give rise to any change of entropy : we have therefore proved that all pure states have the same entropy.

It is now easy to evaluate the increase of entropy associated with the transformation of a pure state ψ into the mixture resulting from the measurement of a quantity with eigenfunctions φ_i. The statistical operator of the mixture is

$$U = \sum_i \varpi_i P_{\varphi_i} \quad , \qquad \text{with } \varpi_i = |(\psi, \varphi_i)|^2$$

i,e. the mixture contains a fraction ϖ_i of states φ_i. In order to find the entropy of this mixture we must try to produce it in a quasi static way, starting from an assembly of systems all in state ψ. To this end, let us divide the N systems of the assembly into groups of $\varpi_1 N$, $\varpi_2 N$,... systems. As we have just seen, we may without change of entropy transform each of these groups into the corresponding pure state fraction of the mixture U, i.e. the i-th group into $\varpi_i N$ systems all in state We have then only to mix together in a quasi static way, all the separate groups thus obtained : this last operation, as is well-known, is accompanied by an increase of entropy,

$$-N \sum_i \varpi_i \log \varpi_i ,$$

i.e. if the entropy is referred to a single system, just the expression (18).

Chapter IV.- Statistics of open systems.

1.- Quantal systems of identical elements. Consider a system of N identical elements. Any physical quantity pertaining to this system is symmetrical with respect to the sets of coordinates representing the elements. This symmetry entails an essential degeneracy of the corresponding operator : from any eigenfunction a set of N! distinct eigenfunctions can be constructed by permuting the coordinates of the N elements in all possible ways; all theses eigenfunctions belong to the same eigenvalue of the operator. In particular, the Hamiltonian presents this degeneracy, which is the analogue in quantum theory of the set of specific phases constituting a generic phase.

The symetry degeneracy is removed, however, by an additional requirement imposed upon all state vectors of the system : these vectors must be either symmetrical or antisymmetrical in the coordinates of the identical elements. By means of any set of N! eigenfunctions of the kind just described one can construct only one symmetrical and one antisymmetrical combination : the one or the other must be chosen according to the nature of the elements. The requirement of antisymmetry is called the exclusion principle; since it implies that no two elements can have the same set of coordinates. The exclusion principle applies, in particular, to the fundamental constituents of matter, nucleons and electrons. It can be shown that elements composed of nucleons and electrons (such as nuclei or atoms or molecules) have symmetrical or antisymmetrical state vectors according as they contain an even or odd number of constituents.

In discussing quantal systems with a variable number of identical elements, a considerable formal simplification is achieved by treating the numbers of elements in this various possible state as quantal variables. Consider first a single element under the external conditions applying equally to all elements of the system : its behaviour is described by a Hamiltonian, which defines a complete set of non-degenerate stationary states of energies E_k of this element. We may now introduce the operator N_k characterizing the number of elements in state k : its eigenvalues are $N'_k = 0, 1, 2.....$ if the state vectors of the system are symmetrical, or $N'_k = 0, 1$ if the elements obey the exclusion principle. If the interactions between the elements are neglected, the Hamiltonina of the system will take the simple additive form

$$H = \sum_k E_k N_k \qquad (1)$$

valid for an unspecified total number of elements.

Any interaction of the elements between themselves or with other species of elements will effect transitions of the systems between states characterized by different numbers N'_k of elements in their various individual states k. The corresponding operators may be expressed in terms of elementary "annihilation" and " creation" operators a_k, a^+_k whose effect on an eigenvector $\psi(N'_1, N'_2, N'_k \ldots)$ of the variables N_1, $N_2 \ldots$ is defined by the relations

$$a_k \psi(\ldots N'_k \ldots) = \sqrt{N'_k}\, \psi(\ldots N'_k - 1 \ldots)$$

$$a^+_k \psi(\ldots N'_k \ldots) = \sqrt{N'_k + 1}\, \psi(\ldots, N'_k + 1, \ldots)$$

in the case of symmetrical state vectors, and

$$a_k \psi(\ldots N'_k \ldots) = N'_k\, \psi(\ldots 1 - N'_k \ldots)$$

$$a^+_k \psi(\ldots N'_k \ldots) = (1 - N'_k)\, \psi(\ldots 1 - N'_k \ldots)$$

in the case of antisymmetrical state vectors. In both cases, the operator N_k is given by

$$N_k = a^+_k a_k$$

The interaction Hamiltonian of the system may consist of various terms representing interactions between pairs, triples, etc... of elements. Thus, the interaction between pairs of elements has a Hamiltonian of the form

$$\sum_{k, \ell, k', \ell'} a^+_k a^+_\ell \, (k\ell \,|\, V(P^{(1)}, P^{(2)}) \,|\, k'\ell')\, a_{k'} a_{\ell'}$$

where $V(P^{(1)}, P^{(2)})$ denotes the operator of potential energy between two elements of coordinates $P^{(1)}$, $P^{(2)}$; the matrice element of this operator must be taken between the two inital states k', ℓ' and the two final states k, ℓ . In the following we shall only discuss in detail systems with weak interactions, for which the simple formula (1) is a sufficient approximation to the Hamiltonian. But in general we may always regard the Hamiltonian operator as a function of the operator a_k, a^+_k, acting upon state vectors of the type $\psi(N'_1, N'_2, \ldots N'_k, \ldots)$

2.- Grand canonical distribution. The classical argument leading to the establishment of the grand canonical distribution for open systems

can be extended to quantal systmes with no essential alteration. The system S under investigation will be described by an Hamiltonian $H(a_k^{(i)}, a_k^{(i)+}, a_k^{(i)}, a_k^{(i)+}; \ldots ; \rho)$ where the operators $a_k^{(i)}$, $a_k^{(i)+}$ pertain to the i-th species of elements contained in the system. The total number of such elements is an operator

$$N^{(i)} = \sum_k N_k^{(i)}$$

We further introduce reservoirs $R^{(i)}$ of elements of each species; their respective Hamiltonians will be $H^{(i)}(b_\ell^{(i)}, b_\ell^{(i)+}, \rho^{(i)})$ where the operators are denoted by $b_\ell^{(i)}$, $b_\ell^{(i)+}$ to indicate annihilation and creation that they refer to elements in different external conditions from those of the system : the a's and b's commute. The numbers of elements in the states of the i-th reservoir will be denoted by $M_\ell^{(i)} = b_\ell^{(i)+} b_\ell^{(i)}$; their total number is accordingly $M^{(i)} = \sum_\ell M_\ell^{(i)}$. The total system consisting of system S and reservoirs may be regarded as a closed system, with fixed numbers

$$\mathcal{N}^{(i)} = N^{(i)} + M^{(i)} \qquad (2)$$

of elements of each species.

The statistical operator of the total system is that of a canonical distribution, $\sim \exp\left[-\beta (H + \sum_i H^{(i)})\right]$; the normalization is obtained by taking the trace of this operator with respect to the set of eigenvectors $\psi (N_k^{(i)'} M_\ell^{(i)'})$ of the numbers of elements in the various possible states, subject to the restrictions (2). The statistical operator pertaining to the system S is accordingly

$$\sim e^{-\beta H} \prod_i \mathrm{tr}\left[e^{-\beta H^{(i)}}\right]$$

where the traces over the reservoir operators are again taken subject to the relations (2); this means that the resulting factors are operators depending on the $N^{(i)}$. At this stage, the argument of the classical treatment which determines the type of dependance of $\mathrm{tr}\left[e^{-\beta H^{(i)}}\right]$ on $N^{(i)}$ can be taken over. In general, for any closed system of M elements, the extensive character of the free energy leads to a proportionality relation

$$\log \mathrm{tr}\left[e^{-\beta H}\right] \sim M$$

Hence, for a very large open system, the variation of $\log \mathrm{tr}\left[e^{-\beta H}\right]$ for a small variation of the number of elements from its average value will be approximately proportionnal to this variation. For the reservoirs we may therefore write, on account of (2)

$$\mathrm{Tr}\left[e^{-\beta H^{(i)}}\right] = e^{\zeta^{(i)} N^{(i)}}$$

where $\zeta^{(i)}$ is a function of the macroscopic variables, including the average numbers $\overline{N}^{(i)}$ ($i = 1, 2, \ldots$). This gives the final form of the statistical operator of the open system S :

$$U_\beta = e^{\beta\{\Omega + \sum_i \zeta^{(i)} N^{(i)} - H\}} \qquad (3)$$

in this formula, the normalization factor $e^{\beta\Omega}$ is defined by

$$e^{-\beta\Omega} = \mathrm{Tr}\left\{ e^{\beta\left[\sum_i \zeta^{(i)} N^{(i)} - H\right]} \right\}; \qquad (4)$$

all quantal operators $N^{(i)}$, H are expressed in terms of the $N^{(i)}_k$, or more generally of the $a^{(i)}_k$, $a^{(i)+}_k$.

If the pressure p is chosen as the external mechanical parameter, we again find that Ω pratically reduces to zero. But it will be more convenient, in the following, to take the volume V as independent variable : then, just as in classical theory, Ω defined by (4) plays the part of a characteristic function $\Omega(\theta, V, \zeta^{(i)})$. It will be noticed that no mention has been made, in the preceding considerations, of the distinction, so important in classical theory, between specific and generic phases : this is simply because the quantal states as explained in § 1, always refer to generic phases; no factors $(N^{(1)}!)^{-1}$ appear explicitely because the reduction to generic phases is already included fro the beginning in the specification of the symmetry or antisymmetry of the state vectors.

3.- Open systems with weak interaction. We shall now apply our general formulae (3) and (4) to open systems with weak interactions. For the moment, we consider systems with only one species of elements : there is then in (3) and (4) no summation over this index (i), which may be dropped altogether. The Hamiltonian is of the additive type (1). We first discuss the thermodynamics of such systems, which is entirely contained in the characteristic function (4). This function can now be put into a form involving only the states E_k of a single element : a transformation which is the analogue of the passage from Γ-space to μ - space in classical theory. In fact, we may write

$$e^{-\beta\Omega} = \sum_{N'_1 N'_2 \ldots} e^{\beta \sum_k (\zeta - E_k) N'_k}$$

$$= \prod_k \sum_{N'_k} e^{\beta(\zeta - E_k) N'_k}$$

For systems with symmetrical state vectors, we must sum over all integral values of the N'_k; this gives

$$e^{-\beta\Omega} = \prod_k \frac{1}{1 - e^{\beta(\zeta - E_k)}} ;$$

for systems with antisymmetrical state vectors, we have only $N'_k = 0$ or 1, whence

$$e^{-\beta\Omega} = \prod_k \left[1 + e^{\beta(\zeta - E_k)}\right]$$

It will be convenient to condense the formulae corresponding to these two cases by introducing the symbol

$$\varepsilon = \begin{cases} +1 & \text{in the antisymmetrical case} \\ -1 & \text{in the symmetrical case} \end{cases} \qquad (5)$$

With this notation

$$-\beta\Omega = \sum_k \varepsilon \log\left[1 + \varepsilon e^{\beta(\zeta - E_k)}\right] \qquad (6)$$

The average number of elements is given by

$$\bar{N} = -\frac{\partial\Omega}{\partial\zeta}$$

i.e.

$$\bar{N} = \sum_k \frac{1}{e^{-\beta(\zeta - E_k)} + \varepsilon} \qquad (7)$$

If the average number $\bar{N}$ is given, equation (7) is an implicit definition of the chemical potential ζ in terms of the macroscopic variables. Since in any case $\bar{N}$ must not be negative, formulae (7) shows that the range of possible values of ζ is restricted in the symmetrical case to $\zeta \leq 0$, while there is no restriction to ζ in the antisymmetrical case. Moreover, one observes that if $\beta\zeta$ becomes negative and very large, the expression for $\bar{N}$ reduces to an asymptotic form common to both kinds of elements :

$$\bar{N} \simeq \sum_k e^{\beta(\zeta - E_k)} \qquad (8)$$

This formula has the same structures as the classical one*, the only diffe-

---

*From the classical formula for an open system with weak interaction

$$e^{-\beta\Omega} = \sum_N \frac{1}{N!} e^{\beta\zeta N} Z^N$$

where Z denotes the sum over the states in μ-space, one derives

$$\bar{N} = -\frac{\partial\Omega}{\partial\zeta} = e^{\beta\Omega} \sum_N \frac{1}{(N-1)!} e^{\beta\zeta N} Z^N$$

The substitution $N \to N + 1$ in the sum over N shows that this sum is equal to

$$e^{-\beta\Omega} e^{\beta\zeta} Z$$

whence $\bar{N} = e^{\beta\zeta} Z$

rence being that the classical expression for the "sum over state" in μ -space is replaced by the corresponding quantal expression

$$Z = \sum_k e^{-\beta E_k} . \qquad (9)$$

One usually expresses this situation, in a somewhat loose terminology, by saying that the limiting case of large nagative $\beta\zeta$ is that of "classical statistics". The general case is then described as that of "quantal degeneracy", and the formulae applying to systems with symmetrical or antisymmetrical state vectors are denoted as "Bose-Einstein or Fermi-Dirac statistics" respectively; the constituent elements of such systems are often called "bosons" or "fermions". The limit of "strong degeneracy", opposed to that of classical statistics, corresponds to $\beta\zeta \simeq 0$ for systems of bosons, and $\beta\zeta \to \infty$ for systems of fermions.

It will be useful to examine somewhat more closely the formula (9) for the sum over states Z. It may be split into two factors, Z_t and Z_i reffering to the degreees of freedom of translation and internal motion, respectively. The factor Z_t can be evaluated in a quite general way. The momentum of an element is related to the wave number of the corresponding stationnary de Broglie wave by the relation $\vec{p} = h\vec{k}$, and the wave numbers are quantized according to the relations

$$k_x = n_x / 2L , \ldots ,$$

where n_x, n_y, n_z are positive integers, and L is the side of a large cube in which the system is assumed to be enclosed. This gives in the usual way the asymptotic expression for the element of measure in momentum space :

$$d\mu_p = \frac{1}{8} dn_x dn_y dn_z = L^3 dk_x dk_y dk_z = \frac{V}{h^3} dp_x dp_y dp_z$$

We get accordingly, if m denotes the mass of an element

$$Z \simeq \int d\mu_p \, e^{-\frac{\beta}{2m}(p_x^2 + p_y^2 + p_z^2)} = \frac{(2\pi m)^{3/2}}{h^3} V \theta^{3/2} \qquad (10)$$

this differs from the classical value only by the constant factor h^{-3}. Such a factor has no influence, in the classical limit, on the thermodynamical significance of the sum over the states, we shall come back in the next section to its physical meaning in quantum theory.

The other factor Z_i of Z depends on the structure of the

elements of the system and cannot be reduced to any universal form. Let ε_0 be the (negative) eigenvalue of the energy of the ground state of an element, and ε_1, ε_2, ... the energies of the successive excited states; the positive difference $\varepsilon_k - \varepsilon_0$ accordingly represent the energy quanta corresponding to the transitions from the excited states to the ground state. We may write

$$Z_i = e^{\beta|\varepsilon_0|} \sum_{k=0}^{\infty} e^{-\beta(\varepsilon_k - \varepsilon_0)} \qquad (11)$$

a convenient form to study the behaviour of Z_i with varying temperature. We see that at very low temperature, Z_i becomes exponentially infinite, like $e^{\beta|\varepsilon_0|}$; at high temperatures, Z_i also tends to infinity, generally like some power of the temperature. For instance, if the element considered performs harmonic oscillations of frequency ν about an equilibrium configuration of energy ε'_0, we have, with $\varepsilon_0 = \varepsilon'_0 - \frac{1}{2} h\nu$

$$Z_i = e^{\beta|\varepsilon_0|} \left[1 - e^{-\beta h\nu}\right]^{-1},$$

and therefore

$$Z_i \approx \theta/h\nu \quad \text{for} \quad \theta/h\nu \gg 1.$$

We are now in position to discuss under which physical conditions the limit of "classical statistics" is valid. According to formula (8), the formal condition for the validity of classical statistics , viz $-\beta\zeta \gg 1$, means

$$\log \frac{Z}{N} \gg 1 \quad , \qquad (12)$$

Let us first treat the cause of elements without internal structure, for which Z reduces to the translation part Z_t. Using formula (10), we may then write the condition (12) in the form

$$\log \left\{ \frac{(2\pi m)^{3/2}}{h^3} \cdot \frac{\theta}{(\bar{N}/V)} \right\} \gg 1 \qquad (13)$$

which shows that "classical" statistics applies at sufficiently high temperatures or low densities. Conversely, we shall expect quantal degeneracy at low temperatures or high densities.

This conclusion is not modified if we include the internal structure of the elements. In fact, returning to formula (7), and putting

$E'_k = E_k - \varepsilon_0$, we derive from it the asymptotic form

$$\bar{N} \simeq e^{\beta(\zeta - \varepsilon_0)} \sum_k e^{-\beta E'_k}$$

identical with (8), on the condition that $-\beta(\zeta + |\varepsilon_0|) \gg 1$, which is slighty more stringent for the absolute value of ζ that our previous condition $-\beta\zeta \gg 1$. But then, according to (11) we get instead of (12) the condition

$$\log \frac{Z_c \cdot Z_i \, e^{-\beta|\varepsilon_0|}}{\bar{N}} \gg 1$$

in which the factor $e^{\beta|\varepsilon_0|}$ which renders Z_i singular at low temperatures neutralized. The only modification in the final formula (13) is therefore an alteration of the exponent of θ in the limiting case of large θ. The qualitative statement of the conditions for the validity of classical statistics remains the same.

4.- Chemical equilibria. As is well known, the two laws of thermodynamics do not suffice to fix completely the law of equilibrium of a system of several constituents in chemical reaction with each other. It is possible to derive by thermodynamical reasoning the general form of hte "law of mass action", but in the expression for this law a constant factor remains undetermined. This arises from the fact that the characteristic functions are only defined up to a linear function of the temperature (a constant for the entropy). In order to remedy thie defect, Nernst was led to supplement the classical scheme of thermodynamics by a further postulate which he called the third law. Nernst's postulate does not directly fix the value of the entropy constant; but it sets up a relation of universal character between the entropies of different systems, which suffices to remove any ambiguity from the law of mass action. Nernst assumes that when the temperature tends to the absolute zero, the entropies of all bodies tend to become equal.

The true significance of Nernst's postulate has only been revealed by quantum theory. In fact, ist validity is a direct consequence of the existence of stationary states, which we can always assume to form a discrete sequence. As the temperature tends to zero, the statistical distribution of any system will tend to be concentrated in its ground state, and according to our quantal definition the corresponding entropy will tend to zero, independently of the nature of the system.

This does not mean that we have derived Nernst's postulate from quantal statistics : for we might of course have added an arbitrary constant to our entropy definition. But we may say that Nernst's postulate fits in quite naturally in the frame of quantum theory : it has no longer the appearance of an ad hoc requirement, but it seen to be intimately connected the existence of stationary states expressed by Bohr's fundamental postulate of quantum theory.

From the preceding considerations it follows immediately that in order to get a complete determination of the law of mass action all we have to do is to stick to the definition we have adopted for the free energy, i.e. to consider this definition as "absolute", without any addition of a linear function of the temperature. Now, our definition consists in relating the free energy directly to the normalization factor of the statistical distribution of equilibrium. This means, precisely, that we take as the "unnormalized" statistical operator that factor which contains the atomistic operators (which we would call classically the "phase functions" viz. the Hamiltonian and the nimbers of elements : we thus obtain a unique meaning for the normalization factor, and consequently for the characteristic function. In other words, all we have to do to secure the fulfilment of Nernst's postulate is to work consistently with actual probabilities correctly normalized to unity in the sense just explained.

Considering, in particular, the limiting case of "classical statistics" (which covers the most usual applications to chemical reactions), we have just to work with the "absolute" value of the sum over states, as given by the formula (10), to get the precise determination of the "chemical constants" entering into the law of chemical equilibrium This implies that the chemical constants will essentially involve the quantum of action, represented by the factor h^{-3} in (10) and similar factors arising from the sum over states of internal motion Z_i. We here meet with a striking illustration of the essential part played by the quantum of action in chemistry : we are, in fact, reminded that the stability of atoms and molecules can only be understood on the basis of quantum theory.

There are phenomena of an essentially different character

from ordinary chemical reactions, in which elements of various kinds can be created and annihilated ; e.g., in interaction with a radiation field pairs of electrons of opposite signs can be produced or can annihilate into radiation. The statistics of open systems we have developped covers such phenomena as well. Let us consider, as a simple, the equilibrium between positons and negatons; the radiation field can be left out of consideration ; it can be regarded as the "thermostat" supplying all necessary energy. We have now a statistical operator of the general type (3), with two species of elements, which we will distinguish by the indices +, -. The average numbers $\bar{N}_+$, $\bar{N}_-$ are not fixed, but connected by the relation

$$\bar{N}_- - \bar{N}_+ = \text{const.}$$

expressing that the total charge (usually an excess of negatons) is conserved (i.e. that the positrons and negatons appear and vanish in pairs) We have simply to write down the equilibrium condition

$$d\Phi = \frac{\partial \Phi}{\partial \bar{N}_+} d\bar{N}_+ + \frac{\partial \Phi}{\partial \bar{N}_-} d\bar{N}_- = \zeta_+ d\bar{N}_+ + \zeta_- d\bar{N}_- = 0$$

with the additional requirement

$$d\bar{N}_+ - d\bar{N}_- = 0$$

This gives immediately

$$\zeta_+ + \zeta_- = 0$$

the chemical potential of either negatons or the positrons can be chosen arbitrarily; the other is then completely fixed by the above relation. It must be noted that the chemical potentials we have used are not the most appropriate to the present problem : in fact, they are referred to a Hamiltonian representing only the kinetic energy of the particles, whereas we are here concerned with an essentially relativistic effect, for which it is more convenient to use the ordinary relativistic definition of the energy which includes the rest mass. The chemical potential ζ^0 referred to this determination of the Hamiltonian is simply related to the potential ζ by

$$\zeta^0 = \zeta + mc^2$$

so that the equilibrium condition takes the form

$$\zeta^0_+ + \zeta^0_- = 2mc^2 \qquad (14)$$

The astrophysical implications of this relation have been discussed by

Chandrasekhar and Rosenfeld . The most immediate inference is the following : we see from (14) that the positron and negatron systems are in a kind of reciprocal relationship with respect to quantal degeneracy. If (as is the case in white dwarfs) the negaton gas is strongly degenerate, the positon gas is in a state corresponding to classical statistics : it cannot, therefore, essentially modify the stellar equilibrium, which is predominantly determined by the pressure of the degenerate negaton gas.

5. Statistiacl distribution of open systems with weak interactions.

Hitherto we have discussed the thermodynamical consequences of the general statistical operator (3) for open systems with weak interactions. Let us now turn to the more detailed consideration of the statistical distribution itself, or, what amounts to the same, the average value

$$\bar{A} = \mathrm{Sp}\left[A\,\rho\right] \tag{15}$$

of any operator A. If we express A in terms of the operator a_k, a_k^*, it is always possible in principle to eliminate from (15) all reference to the numbers of elements and to reduce $\bar{A}$ to an expression involving only the stationary states of a single element. Just as in the classical case, however a simple result is only obtained for additive quantities of the form

$$A = \sum_i \sum_k A_k^{(i)} N_k^{(i)}$$

To avoid trivial complications, let us take the case of a single species of elements. If A is of the type $A = \sum_k A_k N_k$, we get

$$\bar{A} = e^{\beta\Omega} \sum_k \left\{ A_k \,\mathrm{Sp}\left[N_k\, e^{\beta(\zeta - E_k)N_k}\right] \cdot \prod_{\ell \neq k} \mathrm{Sp}\left[e^{\beta(\zeta - E_\ell)N_\ell}\right] \right\}$$

$$= \sum_k A_k \, \frac{\mathrm{Sp}\left[N_k\, e^{\beta(\zeta - E_k)N_k}\right]}{\mathrm{Sp}\left[e^{\beta(\zeta - E_k)N_k}\right]}$$

This has indded the form of an average over the stationary states of a single element, with a distribution function $f(E_k)$:

$$\bar{A} = \sum_k A_k \, f(E_k) \tag{16}$$

The function $f(E_k)$ represents the average number $\bar{N}_k$ of elements in state k. An explicit expression for it is easily obtained. We start from

$$F(E_k) \equiv \mathrm{tr}\left[e^{\beta(\zeta - E_k) N_k}\right] = \left[1 + \varepsilon\, e^{\beta(\zeta - E_k)}\right]^{-\frac{1}{\varepsilon}}, \tag{17}$$

with the notation (5) for distinguishing bosons and fermions. The distribution function $f(E_k)$ is the logarithmic derivative of $F(E_k)$ with respect to $\beta(\zeta - E_k)$, i.e.

$$f(E_k) = \frac{1}{e^{-\beta(\zeta - E_k)} + \varepsilon} \tag{18}$$

The limiting case of classical statistics requires no special comment; using (8) and (9) to eliminate ζ, we get

$$f(E_k) \simeq \frac{N}{Z}\, e^{-\beta E_k}$$

On the other hand, the behaviour of the distribution for strong quantal degeneracy is quite different for bosons and fermions. In the case of bosons, we shall have an accumulation of elements in the ground state leading to a peculiar "condensation" phenomenon; in the case of fermions the tendency will be for the elements to fill up all the lowest stationary states. A thorough discussion of these aspects, which have physical applications of fundamental importance, is outside the scope of this course.

6. Statistics of the radiation field. The only point which remains to be settled is the position of the radiation field with respect to the statistics of open systems. A radiation field within an enclosure with reflecting walls can be described as a system of independent proper oscillations, whose wave numbers $\vec{k}_i$ are determined by the boundary conditions; moreover, to each wave-number belong two independent modes of polarization. Each proper oscillation [*], of frequency $\nu_i = c\,|\vec{k}_i|$, is quantized as a harmonic oscillator of that frequency, i.e. its energy has the eigenvalues $(N_i + \frac{1}{2})\, E_i$ where $E_i = h\,\nu_i$ and N_i is a non-negative integer. Although there is no interaction between different proper oscillations, the system is nevertheless ergodic, provided that we introduce into the enclosure a "grain of coal dust"

---

[*] The single index i represents the set of quantum numbers characterizing the proper oscillation, including its polarization.

("Kohlestäubchen) to secure by absorption and emission the necessary exchange of energy between the various oscillations. In other words, we treat the radiation field as a closed system of proper oscillations in contact with a thermostat represented by the grain of coal dust.

The total Hamiltonian is simply the sum of the Hamiltonians H_i of the proper oscillations. Leaving out the zero-point energy of the oscillators, we get for the free energy of the systems

$$e^{-\beta F} = \mathrm{tr}\left[e^{-\beta H}\right] = \prod_i \mathrm{tr}\left[e^{-\beta H_i}\right]$$

$$= \prod_i \sum_{N_i} e^{-\beta E_i N_i} = \prod_i \frac{1}{1 - e^{-\beta E_i}},$$

i.e.

$$-\beta F = -\sum_i \log\left[1 - e^{-\beta E_i}\right] \qquad (19)$$

This expression presents a formal analogy with that for the characteristic function Ω of a system of bosons, given by (6) : it would correspond to the value $\zeta = 0$ of the chemical potential.

The bosons in question are the quanta of oscillation of the field, usually called photons : they represent the "particle aspect" of the radiation field. In fact, to each wave number $\vec{k}_i$ and mode of polarization wa may associate photons of energy $E_i = h\nu_i$. Moreover, in virtue of the laws of the radiation field, the proper oscillation has a momentum $N_i E_i/c$ in the direction $\vec{k}_i$: we may thus ascribe to each photon belonging to this oscillation a momentum of magnitude $p_i = E_i/c$ and direction $\vec{k}_i$, i.e. $\vec{p}_i = h\vec{k}_i$; The rest mass of the photon is accordingly zero. We may further introduce creation and annihilation operators for photons, and define the operator N_i for the number of photons in state i. The Hamiltonian of the field then takes the form $H = \sum E_i N_i$, corresponding to a system of particles in weak interaction. In this representation, the radiation field is conceived as an open system of bosons, the grain of coal dust playing the part of a reservoir of photons. Thus, the exchange of energy and the exchange of elements are here the same process, and this circumstance is expressed by the fact that the chemical potential vanishes.

The statistical operator of the radiation field

$$U_\beta = \frac{e^{-\beta H}}{\mathrm{Sp}\left[e^{-\beta H}\right]} \qquad \text{with } H = \sum_i E_i N_i$$

gives rise to a distribution function

$$f(E_k) = \frac{1}{e^{-\beta E_k} - 1}$$

for the computation of averages of operators additive in the photon numbers The asymptotic expression for the element of measure in the momentum space of the photons is twice the usual one, so as to account for the two independent modes of polarization. Thus from (19) we get for the free energy the asymptotic value

$$\begin{aligned} F &= \theta \cdot \frac{8\pi V}{h^3} \int_0^\infty p^2 dp \, \log\left(1 - e^{-\beta c p}\right) \\ &= \frac{8\pi V \theta^4}{(hc)^3} \int_0^\infty x^2 dx \, \log\left(1 - e^{-x}\right) \\ &= -\frac{\sigma}{3} V \theta^4 \qquad \text{with } \sigma = \frac{8\pi}{(hc)^3} \int_0^\infty \frac{x^3 dx}{e^x - 1} \end{aligned}$$

This formula contains the thermodynamics of the radiation field, viz. its entropy density

$$S = \frac{4}{3} \sigma \theta^3 ,$$

its energy density

$$\bar{\mathcal{E}} = \frac{E}{V} = \epsilon \theta^4 \qquad \text{(law of Stefan-Boltzmann)}$$

and the radiation pressure

$$p = 1/3 \; \bar{\mathcal{E}}$$

C O N T E N T S

III.- Statistics of closed systems.

IV.- Statistics of open systems.

QUANTUM STATISTICS.

I.- Quantal description of Physical systems.

II.- The ergodic theorems.

III.- Statistics of closed systems.

IV.- Statistics for open systems.